

MECHANISTIC, MODEL COMPOUND, COPOLYMERIZATION AND
MODIFICATION REACTION STUDIES OF THE 4-SUBSTITUTED-
1,2,4-TRIAZOLINE-3,5-DIONE RING SYSTEM

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1976

This dissertation is dedicated to my parents,
Dr. and Mrs. A.G. Williams and to my wife in appreciation
for their love and support as well as for their inspiration
to my growth by their devotion and care for others.

ACKNOWLEDGEMENTS

My stay at the University of Florida has been a most rewarding experience and I would like to express my gratitude to the many people who have made this experience possible.

I wish to express my appreciation to Dr. G.B. Butler for his friendship and guidance as my research director.

I wish to thank Dr. T.E. Hogen-Esch, Dr. R.C. Stoufer, Dr. William R. Dolbier, and Dr. Michael E. Thomas for giving of their valuable time to serve on my supervisory committee.

I wish to thank Dr. J. Baxter, Dr. R.C. Stoufer and Dr. William R. Dolbier for their contribution of ideals of teaching.

I would also like to extend my sincere thanks to my colleagues in the laboratory who made working more pleasant.

Finally I would like to express my thanks to my wife whose constancy has made it easier to complete this work.

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Abstract of Dissertation Presented to the
Graduate Council of the University of Florida in Partial
Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

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June, 1976

Chairman: Dr. George B. Butler
Major Department: Chemistry

4-Substituted-1,2,4-triazoline-3,5-dione was found to add to the α -position of β -diketones and β -diketoesters yielding both 1:1 and 2:1 (triazolinedione:dicarbonyl) adducts, making the β -dicarbonyls bifunctional with respect to the triazoline-dione addition. The 1:1 adducts showed a dramatic stabilization of the enolic tautomer when compared to the original β -dicarbonyls as evidenced through a large increase in percent enol in all solvents. Kinetic studies support reaction through the 1,4-dipolar pathway involving triazolinedione and the enolic form of the β -dicarbonyl. This reaction was also found to demonstrate a strong solvent dependency, hydrogen bonding solvents being rate enhancing. Low molecular weight copolymers were synthesized employing 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione as a bifunctional triazolinedione.

Polymers containing unsaturation have been modified in a

variety of ways through chemical addition to the unsaturated group. The method enjoying the greatest success is the thermal addition of maleic anhydride, a process which leaves a rearranged double bond. This process, however, requires high temperature and results in low percentage addition. 4-Phenyl-1,2,4-triazoline-3,5-dione has been found to add thermally to polymers such as polybutadiene and polyisoprene. Additions in solution of from 1 to 93 percent (mole triazolinedione:mole repeating unit) were obtained at room temperature. Physical property changes ranged from secondary crosslinking or elasticity at low percentage additions, to a complete change from rubber texture to a soft powder at high percentage additions. The modifications of greater than 45 percent were found to be soluble in weak bases such as 1M NaHCO_3 . Similar reactions employing the bis triazolinedione, 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione resulted in crosslinked polymer.

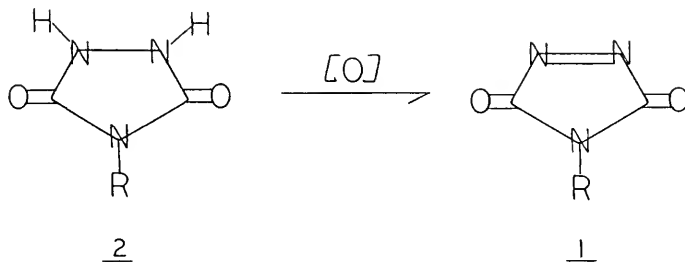
CHAPTER I

INTRODUCTION

A. General Background

Carbonyl azo compounds containing one or two carbonyl functional groups adjacent to the azo group take part in a large variety of reactions and differ from their aliphatic and aromatic counterparts in the reactivity of their N=N functionality.¹⁻¹¹

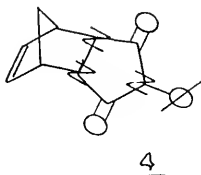
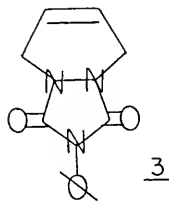
Of particular recent interest has been the utility of a particularly reactive member of this family known as 4-substituted-1,2,4-triazoline-3,5-dione, 1. The synthesis of this compound begins with an isocyanate which determines the four substituent and ends with oxidation of the urazole, 2.



This oxidation can be carried out in a variety of ways: Lead peroxide in cold dilute H_2SO_4 ¹², heavy metal salts of

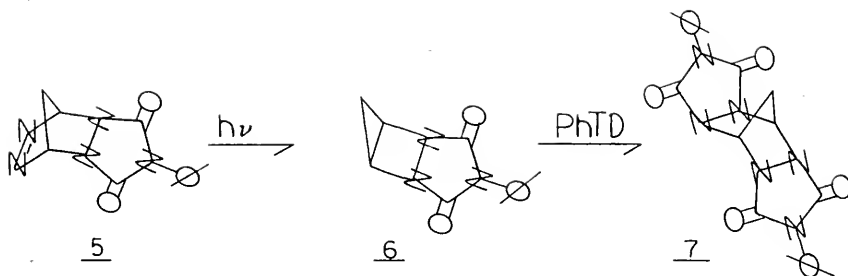
the urazole in reaction with I_2 ,¹³ t-butyl hypochlorite in acetone,¹⁴ lead tetra-acetate in methylene chloride,¹⁵ bromine,¹⁶ fuming nitric acid,¹⁷ manganese dioxide, calcium hypochlorite or NBS,¹⁸ and 1,3-dibromo-5,5-dimethylhydantoin. Purification is usually achieved by solvent evaporation and sublimation. More recent work by J.A. More¹⁹ accomplishes the oxidation and subsequent reaction in-situ. Oxidation is achieved via activated isocyanates such as p-toluenesulfonyl isocyanate in DMSO. Conversion is determined spectrophotometrically.

Reactions with this compound began in strength in the early 1960's with low temperature Diels Alder 4+2 cycloadditions by Cookson, Gilani and Stephens.¹⁴ Here 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD) was treated with butadiene and cyclopentadiene to yield the 1:1 adducts 3 and 4 respectively.

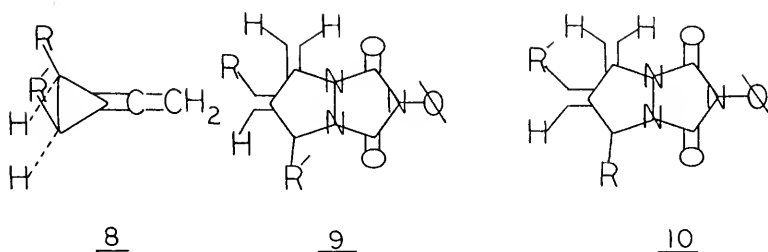


This led to more research with the 4+2 cycloadditions of 1.²⁰⁻²⁵

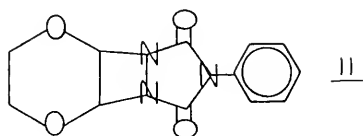
Evnin and Arnold²⁶ reacted PhTD with isopyrazoles to give 5 which on irradiation loses nitrogen to give 6. This subsequently reacts with more PhTD to give the 2:1 adduct 7.



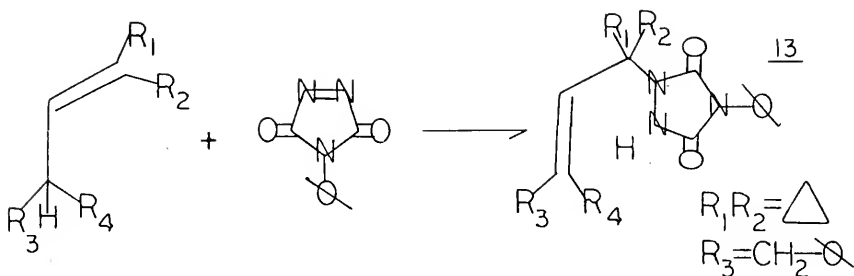
Other 2:1 and 1:1 adducts have been subsequently reported with nitrogen heterocyclic compounds.²⁷⁻³² Additional cycloadditions of 1 include the $[(\alpha^2 + \pi^2) + \pi^2]$ reactions of alkenylidene cyclopropanes. Pasto and Chen,³³ for instance, report the reaction of PhTD and 8 to give 9 and 10. Still others have been reported.³⁴



2+2 Cycloadditions have been reported.³⁵⁻³⁶ Dihydro-1,4-dioxime, for instance, has been reported to form 11 with PhTD.

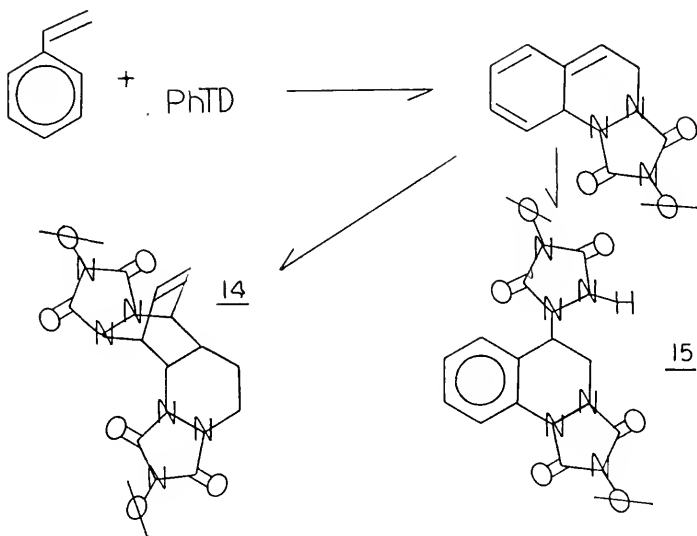


The Diels-ene pathway is also taken with triazolinediones. Pasto and Chen²⁹ first observed this reaction as depicted below.



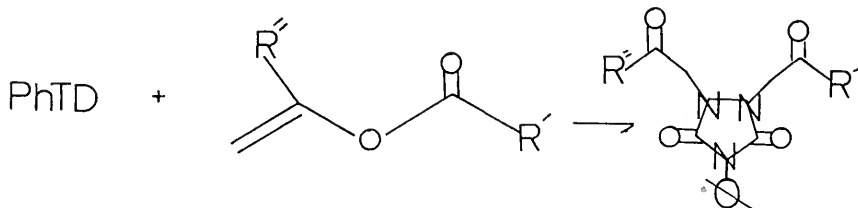
They reacted (4-phenylbutylidene)-cyclopropane with PhTD to form the ene product 13. This reaction was found to be approximately 30,000 times faster than that employing conventional azodicarboxylates.³⁷

Combinations of the reaction pathways have been found in reaction of PhTD and various styrenes. Cookson and Gilani²⁸ found a double Diels Alder adduct 14 with PhTD and styrene.



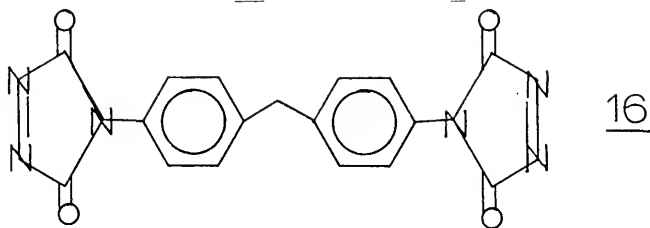
Further investigation by Guilbault, Turner, and Butler³⁸ pointed to both the Double Diels Alder and the Diels Alder-ene (15).

Turner, Guilbault, and Butler³⁹ also found PhTD to undergo an intramolecular rearrangement with vinyl acetates.



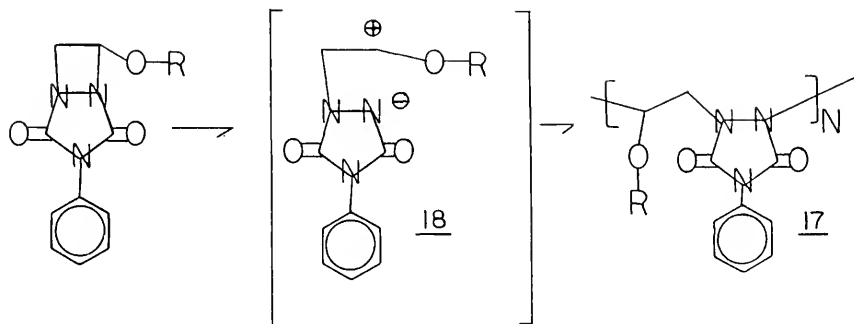
Wagener and Butler⁴⁰ give strong evidence for the existence of a 1,4-dipolar intermediate. This intermediate was also proven in the reaction of PhTD with vinyl ethers.⁴¹⁻⁴²

Copolymerizations have been accomplished employing the bis-triazolinedione, 16, as well as 1.



Wagener⁴¹ reported a copolymer of 16 and divinyl adipate via the rearrangement reaction to give low molecular weight polymers having low solubility. Copolymerization of 16 has also been accomplished via the double Diels Alder and the Diels Alder-ene pathway with styrene yielding high molecular weight polymers.

Turner and Butler⁴¹ reported copolymerization of PhTD and vinyl ethers to give low molecular weight copolymers, 17, via ring opening polymerization of the initially formed 1,4-dipolar adduct, 18.



Other uses of triazolinediones include oxidation of alcohols to aldehydes and ketones⁴³ and oxidation of substituted hydrazines to give N-nitrenes which form an adduct with a second PhTD to give azimes.⁴⁴⁻⁴⁵

Kinetic investigation shows⁴⁶ PhTD as one of the most powerful dienophiles known. It is 10^3 times more reactive than TCNE and 2×10^3 times more reactive than maleic anhydride. This is, undoubtedly, directly responsible for the prolific reaction variations. A significant result of this is the ability of the substituted triazolinediones to react at room temperature, a factor which makes it an excellent dienophile for low reactive and unstable electrocyclic substrates.

B. Research Objectives

To date investigation of the triazolinedione system has been for the most part limited to the monofunctional

study of the compound. Application of these monofunctional reactions into polymerization has taken place as described above for the most part in these laboratories. The objectives of this work have been to further the study of this compound as it may apply to polymerization or polymerization systems. This has been accomplished through two unrelated studies.

The first study concerns the investigation of a new potential copolymer system employing β -diketones. The objectives of this study have been

1. To look at model compound reactions of PhTD with β -diketones to determine their potential as monomers as well as their repeating unit structure.
2. To attempt these copolymerizations with the bis-triazolinedione, 16.

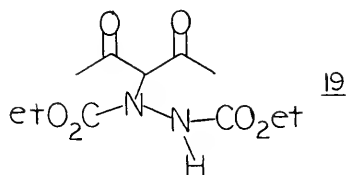
The second study concerns investigation of triazoline-dione as a modifier of existing unsaturated polymers. The objectives of this study have been

1. To synthesize functionalized 4-substituted triazolinediones which could be used as ionic modifiers.
2. Attempt the modification itself and determine its effect on the physical properties of the polydienes employed.
3. Determine the conditions and extent of the modification.

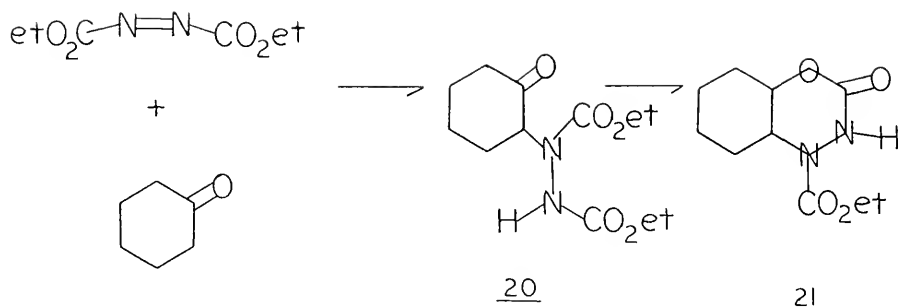
CHAPTER II
SYNTHESIS AND KINETIC STUDY OF ADDUCTS OF β -DIKETONES
AND β -KETOESTERS WITH PhTD

A. Background

Diethyl azodicarboxylate and esters of phenyl azocarboxylic acid react with sodium salts of C-H acids such as acetoacetic ester, cyanoacetic ester and acetylacetone to form substituted hydrazines.⁴⁷⁻⁴⁸ Diethylazodicarboxylate and sodium acetoacetate give the adduct 19 on mixing at room temperature.

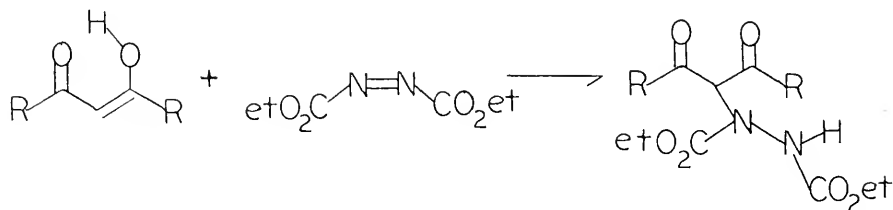


Huisgen and Jakob⁴⁹ isolated 1:1 adducts of azodicarboxylates with various ketones. By use of ethyl azodicarboxylate they were able to show conclusively the formation of the 1:1 adduct 20 with cyclohexanone through subsequent reduction of the carbonyl group, followed by formation of the cyclic urethane 21. "A priori" consideration allows one to see the possibility of addition to the α position by either a free

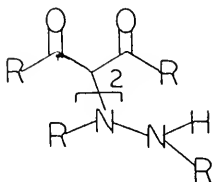


radical or an ionic mechanism due to stabilization effected by the carbonyl group. Radical initiators and inhibitors, respectively, resulted only in a three-fold increase and limited reduction of the rate. It was therefore their belief that the reaction was ionic in character, a belief supported by observed rate increases with acid and heterogeneous base catalysis.

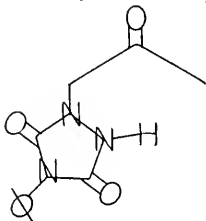
Diels and coworkers⁵⁰⁻⁵¹ observed similar reactions with β -dicarbonyl compounds and suggested reaction through the enolized form of the dicarbonyl compound.



As 4-substituted-1,2,4-triazoline-3,5-diones have been shown to be extremely reactive members of the azodicarbonylate family the possibility of their reaction with β -diketones and β -diketoesters was investigated. The reaction which involves substitution of the α hydrogen with the azo compound, while to date has resulted in only the 1:1 adduct, possesses the potential to add in a 2:1 azo: β -diketone fashion.



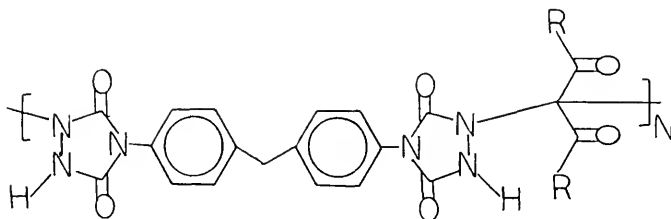
Although this would be expected to be sterically unfavorable, it was assumed to be possible with the cyclic azo compound due to its high reactivity. Ruch⁵² and Cookson²⁸ in separate works reported the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD) with acetone to form 1-hydro-2-acetomethyl-4-phenyl-1,2,4-triazoline-3,5-dione 22.



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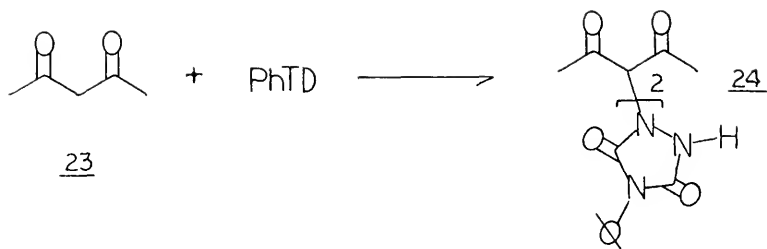
Although no mechanistic study was conducted, Ruch postulated reaction through the extremely low concentration of enolized

acetone as explanation for the relatively slow reaction. Since no investigations dealing with the reaction between triazolinediones and β -dicarbonyls have been published, such studies were initiated in this laboratory. If indeed the 2:1 adduct were possible, β -dicarbonyls would be considered bifunctional and therefore would possess the potential to form copolymers of the structure shown below with a bis triazolinedione such as 16.



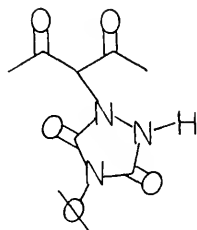
B. Adducts of 2,4-Pentanedione and 4-Phenyl-1,2,4-triazoline-3,5-dione.

2,4-Pentanedione was added to a solution of PhTD in acetonitrile in a molar ratio of 1:1. Reaction was complete in approximately one hour as noted by disappearance of the characteristic red color of the triazolinedione. The solution was rotoevaporated and the solid recrystallized from acetone. NMR and elemental analysis indicated the 2:1 adduct, 24, to be the reaction product. As the 1:1 adduct was also an expected product of this reaction, it was assumed that



2:1 adduct formation was either kinetically or thermodynamically favored. Assuming kinetic preference, a second attempt was made to synthesize the 1:1 adduct. The reactants were mixed as before in acetonitrile employing a 4:1 excess of 2,4-pentanedione. The reaction was complete in fifteen minutes. Subsequent workup resulted in a stable white powder which was recrystallized from ethanol-water. Elemental and mass spectral analysis of the compound indicated 25 to be the structure.

25



The NMR (figure 1) spectrum, however, showed no α -proton absorption and a marked shift of the pendent methyl signals upfield (in DMSO- d_6) from 145cps to 115cps. Further inspection showed a broad band at 16.0 δ which by integration was

168

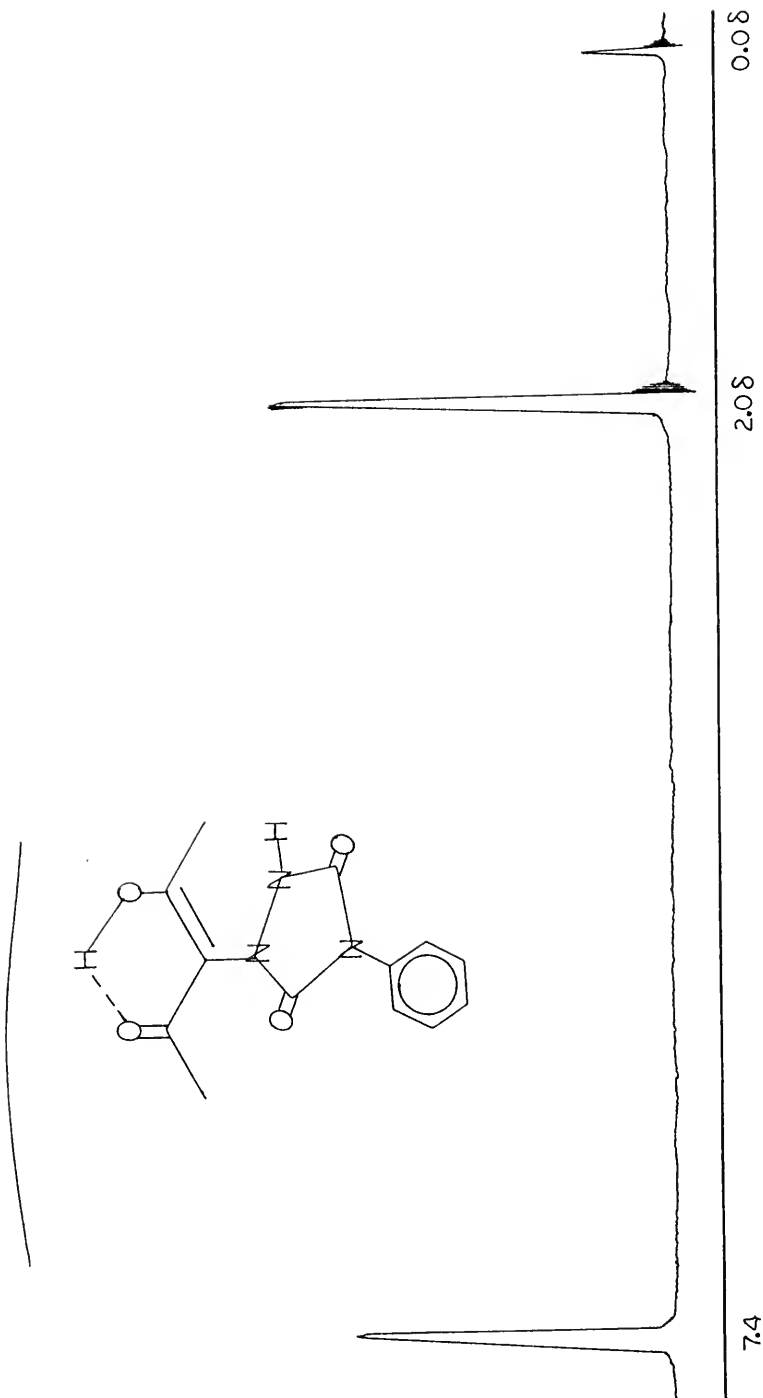
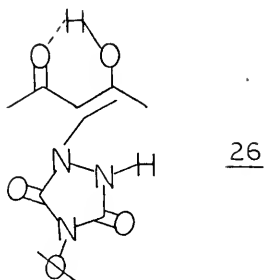
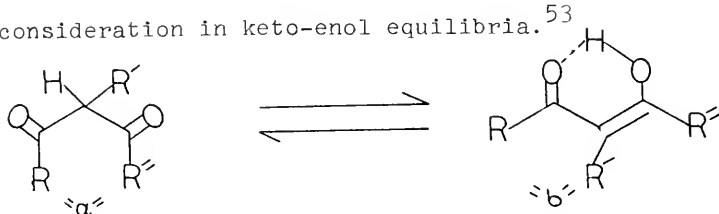


FIGURE 1. Nuclear Magnetic Resonance Spectrum of 2-(2-Hydroxy-4-phenyl-1,2,4-triazoline-3,5-dione, 26).

shown to be equivalent to one proton. The shift in the methyl absorption and appearance of the peak at 16.0 δ are both indicative of a highly stabilized β -dicarbonyl enol tautomer. Infrared (ir) absorption characteristic of a chelated enol is found at 1640 cm^{-1} . Ultraviolet spectral analysis (UV) likewise supports this conclusion as a characteristic chelated absorption was observed at 272 nm. This information allows assignment of 26 as the structure of the 1:1 product.



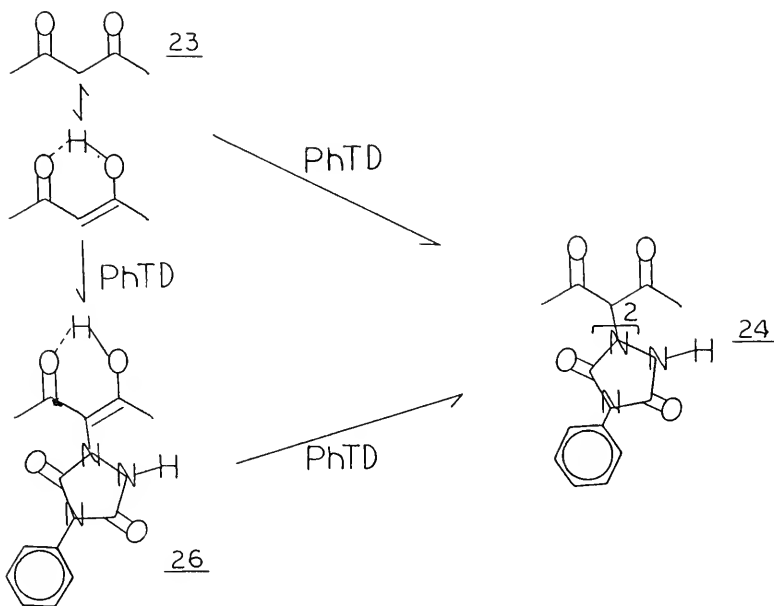
The percentage of enolization of β -dicarbonyls is known to be solvent dependent, more polar hydrogen bonding solvents being the most suppressive. The absence of an α -proton absorption in DMSO implies this adduct to be essentially 100% enolized in all solvent systems. For β -diketones the nonbonded Van der Waals interaction between R and R' is an important consideration in keto-enol equilibria.⁵³



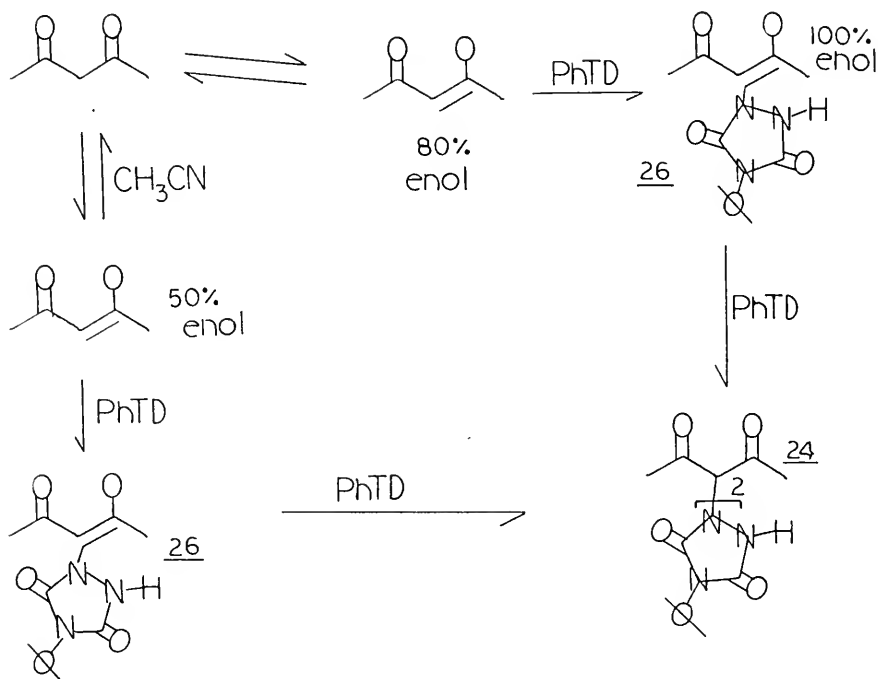
As a result equilibrium favors the enol tautomer. Examination of models indicates no steric interaction with the 1:1 adduct 25 in either tautomer "a" or "b". The stabilization resulting from the chelation and conjugation is therefore assumed to be increased through the electron-withdrawing nature of the α -substituted urazole resulting in the observed tendency toward formation of the enol tautomer relative to the pure β -diketone.

C. Mechanistic Study of the β -Diketone-PhTD Reaction.

Reaction of equimolar quantities of the 1:1 adduct 26 with PhTD resulted in quantitative formation of the 2:1 adduct, 24. The following reaction pathway can then be envisioned:



This finding implies that reaction occurs through the enol tautomer in formation of the adducts as formation of the 2:1 adduct from the 1:1 adduct apparently takes place through this route. Adduct reaction rates with various other β -diketones and β -ketoesters to be discussed later in this chapter, were found to be dependent on the amount of enol initially present in the diketone. As a means of supporting this theory, 2,4-pentanedione was reacted with PhTD in a 1:1 molar ratio in methylene chloride, ethyl acetate and acetonitrile. The percent enolization in these solvents was found to be 80-70-45 percent, respectively, as determined by NMR. Similar NMR studies of the 1:1 adduct in these solvents show it to have the expected 100% enolization. The following scheme is then considered:



Assuming the enolic form of the β -diketone to be the reacting species the amount of 1:1 adduct versus 2:1 adduct formed in this reaction could be a function of the ratio of enolic content for 2,4-pentanedione and the 1:1 adduct, 26, in a particular solvent. Formation of 2:1 adduct 24 would therefore be favored in solvents decreasing this ratio due to an increase in probability of PhTD encountering a reactive form, the enol, with the 1:1 adduct due to its complete enolization in the solvents studied. Reaction occurring through the keto form would be expected to reverse these product ratios. This argument also assumes the relative rates of 1:1 and 2:1 adduct formation remains the same in each solvent.

TABLE I

Adduct Ratios of PhTD-2,4-pentanedione Reaction

SOLVENT	REACTANT RATIO ²	% ENOL ¹	% 2:1 ADDUCT
CH ₂ Cl ₂	1:1	80	17
EtAc	1:1	70	40
CH ₃ CN	1:1	50	95

¹ Based on NMR integration of 2,4-pentanedione

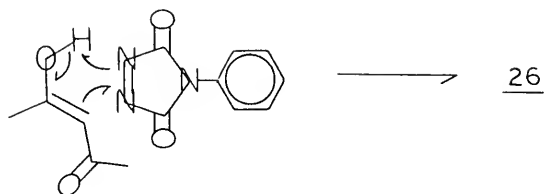
² β -diketone:PhTD

As Table I shows the relationship between the 1:1 and 2:1 adducts under the various conditions employed are as expected giving support to the theory of reaction through an enolic substrate.

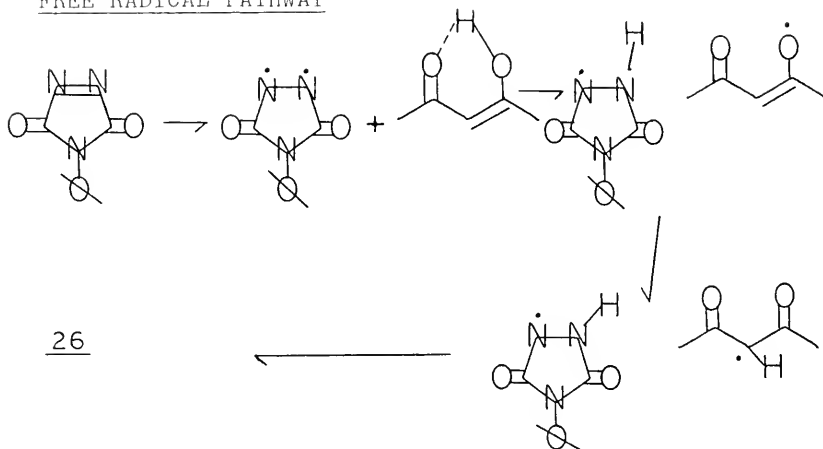
Possible mechanisms

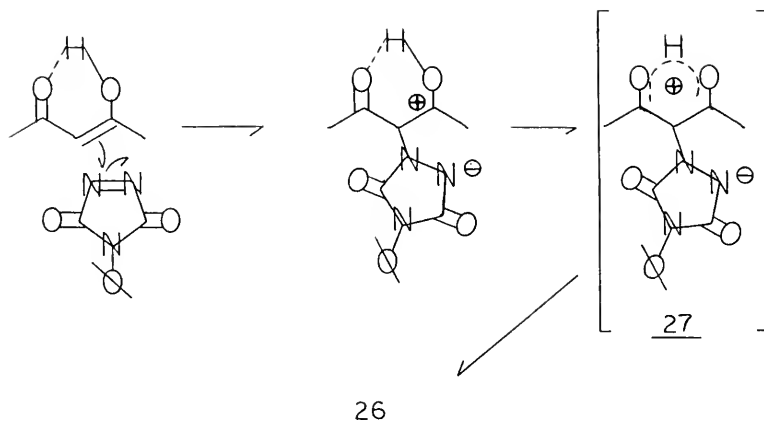
In an attempt to postulate the most probable mechanism, the possible reaction pathways for an enolic substrate were considered and subsequently compared to kinetic and spectral information obtained. Three potential reaction pathways can be rationalized..

ENE PATHWAY



FREE RADICAL PATHWAY



1-4 DTPOLAR PATHWAY

The ene and dipolar pathways would be expected to proceed via second order kinetics with the free radical yielding a complex kinetic scheme. In an attempt to obtain kinetic data on the system, the reaction of PhTD and the 1:1 adduct, 26, was studied spectroscopically monitoring the PhTD visible absorbance in $(\text{CHCl}_2)_2$ at 545 nanometers. Application of the data obtained to the second order equation gives a rate of $1.072 \times 10^{-3} \text{ l-mole}^{-1}\text{-sec}^{-1}$ by the least squares method ($\text{COC} = .9997$). This reaction was chosen for the kinetic work due to the singular product it affords, namely the 2:1 adduct, 24. Subsequent kinetic studies undertaken to determine possible solvent effects (Table II) indicate an unusually strong solvent dependency for the system. The rate change from slowest to fastest is approximately 70,000, a finding difficult to explain in terms of the ene

TABLE II
ROOM TEMPERATURE KINETICS OF PhTD AND 26

SOLVENT	$K(1\text{-mole}^{-1}\text{-sec}^{-1})^2$	COC	SOLVENT DIPOLE
THF ³	70.5	.978 ¹	1.63
1,4-Dioxane	13.29	.999	0.00
EtAc	2.60	.999	1.78
$(\text{CHCl}_2)_2$	1.07×10^{-3}	.999	1.32

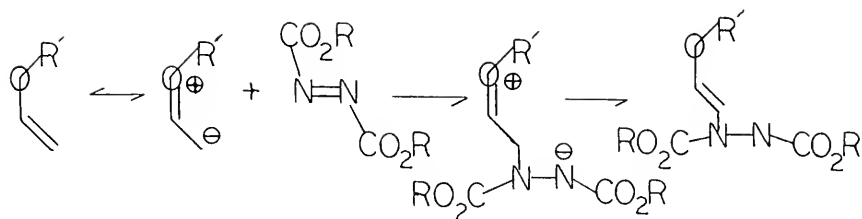
¹ Poor COC attributed to rapid reaction relative to mixing.

² Calculated by method of least squares.

³ Distilled fresh from Na.

reaction. As an electrocyclic concerted reaction, the ene reaction is characterized as a "no mechanism" path and as such is not expected to be dramatically affected by solvent changes. Wagener⁵⁴ noted a small solvent influence in the Diels Alder-ene reaction of PhTD with styrene. This rate influence was of low magnitude and opposite to that observed with this reaction system. Work described in Chapter III verified this conclusion as the reaction of PhTD and 4-methyl-1-pentene giving the 1:1 ene adduct is found to have a similar change with solvents. The ene reaction mechanism, therefore, appears to be an unlikely choice as the most probable mechanism for these adduct formations and was ruled out.

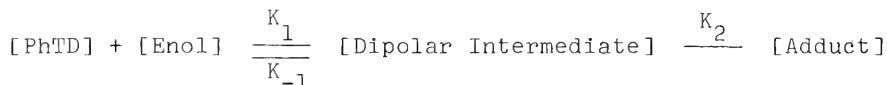
Esters of azodicarboxylic acid undergo reaction with vinyl ethers⁵⁵⁻⁵⁶ through a dipolar intermediate as depicted below:



Butler, Wagener and Turner^{40,42} give substantial evidence for a similar reaction pathway with PhTD and vinyl ethers and esters. It is generally thought that dipolar reactions should show pronounced solvent effects. The results of a solvent study of the vinyl ethers⁴² with PhTD show no correlation with solvent polarity. Since both monomers were highly polar, it was reasoned that they could experience enough ground state solvation to effectively cause the solvation of the intermediate to be undetectable. It, therefore, is plausible to suspect a similar mechanism with the β -diketone system. As Table II shows, the rate does not parallel solvent polarity. The greatly enhanced rate would, at best, be difficult to explain simply by polarity stabilization in view of Turner's evidence.

Enol tautomers exist in the hydrogen bonded species for both 2,4-pentanedione and the 1:1 adduct, 26. Wheland⁵⁷ estimates that the intramolecular hydrogen bond of pentanedione stabilizes the enol tautomer by 5-10 kcal and the conjugated system further stabilizes this by 2-3 kcal. The

effect of a substitution of an electron withdrawing substituent to this has been shown by Z. Yoshida et al.⁵⁸ to increase this stabilization, and barring steric difficulties, to increase the percentage of enol in the adduct. If the intermediate, 27, shown in the 1,4-dipolar pathway above, shares this stability, its decay would have an influence on the overall reaction rate. Making this assumption the following kinetic scheme was proposed.



Steady state treatment of the intermediate results in

$$[\text{Intermediate}] = \frac{\text{K}_1 [\text{PhTD}] [\text{Enol}]}{\text{K}_{-1} + \text{K}_2}$$

$$\text{Rate} = \text{K}_2 [\text{Intermediate}]$$

$$= \frac{\text{K}_1 \text{K}_2}{\text{K}_{-1} + \text{K}_2} [\text{PhTD}] [\text{Enol}]$$

$$\text{K}' \text{K}_2 [\text{PhTD}] [\text{Enol}], \text{ where } \text{K}' = \frac{\text{K}_1}{\text{K}_{-1} + \text{K}_2}$$

A study of the chemical shift of the enolic OH (Table III) shows a small deviation upfield as the H-bonding tendency of the solvent increases. We assume, therefore, the function of oxygen-containing solvents in the observed rate increase is two-fold, (1) weakening the intermediate, 27,

allowing it to collapse to product and (2) acting as a transfer agent for the proton from the weakened chelate to the amide position.

TABLE III
CHEMICAL SHIFTS OF CHELATED ENOLIC PROTON OF 26 AND 32

SOLVENT	ENOLIC SYSTEM	CHEMICAL SHIFT
Acetone	26	950 cps
DMSO	26	670 cps
(CHCl ₂) ₂	26	970 cps
Dioxane	26	900 cps
CHCl ₃	26	960 cps
(CHCl ₂) ₂	32	780 cps
THF	32	720 cps

To test this theory a system was needed which would not be expected to display this type of solvent dependency. This required that it not be capable of forming the stabilizing chelation and exist completely in the free enolic form. Such a diketone, 1,3-cyclohexanedione, 28, is prevented from the intramolecular chelation due to the methylene bridge. NMR provides proof of this in the appearance of the OH chemical shift at 10 δ as a sharp singlet in chloroform. The methylene bridge and 1,3-dicarbonyl moiety force the carbonyl groups and α -carbon into coplanarity allowing the compound to exist in a resonance stabilized enolic state which is 100% in most solvents. Stabilization of the intermediate

formed from reaction of this compound with PhTD cannot be a factor in its kinetics. The solvent may exert an effect only if it is acting as a proton transfer agent. A comparison of the rates of 23 and PhTD in THF and $(\text{CHCl}_2)_2$ with those of 28 and PhTD in the same solvents should show a dramatic variance in the differential solvent rates. The overall rate would also be expected to be high for the unstabilized system.

In order to preclude any steric problems with 1:1 → 2:1 reaction, the reaction chosen for this study was that of the pure diketones, 23 and 28, with PhTD. As both the 2:1 and 1:1 adducts may form under conditions employed for the secondary rate determination, pseudo first order rate conditions employing a 10-fold excess diketone were used. Trial reactions were run under these conditions. After complete reaction, solvent was stripped away and the crude solid analyzed with NMR. No indication of the 2:1 adduct was found.

For each of the four systems, two ml volumetric flasks were prepared. The one containing PhTD was added to the sample vial. The diketone was injected with sufficient force to effect mixing of the two reactants. The THF run with 2,4-pentanedione was too rapid to follow accurately, making it necessary to make a conservative estimate of the rate based on data obtained. To assure this reaction was indeed following the kinetics of the other samples its rate was measured at a depressed temperature (5°C) and found to give the desired correlation to first order equation. Table IV

shows the expected decrease in solvent dependency for 1,3-cyclohexanedione.

TABLE IV

SOLVENT DEPENDENCY OF PSEUDO 1st ORDER KINETICS FOR PhTD
ADDUCTS OF 1,3-CYCLOHEXANEDIONE & 2,4-PENTANEDIONE

SYSTEM	SOLVENT	K(sec ⁻¹)	DELTA K	COC
23 + PhTD	(CHCl ₂) ₂	1.10 x 10 ⁻⁴	1000	.9996
23 + PhTD	THF	10 ⁻¹		
28 + PhTD	(CHCl ₂) ₂	9.50 x 10 ⁻³	5.6	.9997
28 + PhTD	THF	5.33 x 10 ⁻²		

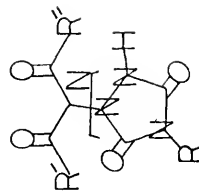
D. Adducts of PhTD with β -Diketones and β -Diketoesters.

Having established an enol monomer which increases its ability to add the triazolinedione moiety in formation of the 1:1 addition product by increasing the percentage of reactive species, namely the enolized ketone, other β -dicarbonyls were studied to determine if this trend would be found. Those employed in this study along with the adducts are listed in Table V.

Adducts of ethyl acetoacetate (31) with PhTD

Treatment of 0.0034 moles PhTD with 0.0034 moles ethylacetoacetate in methylene chloride gives complete decoloration in 24 hours. Analysis and spectral data show the 2:1 adduct, 33, to be obtained in 60% yield after recrystallization. As ethylacetoacetate is only 7% enolized in this

TABLE V

ADDUCTS OF THE 4-SUBSTITUTED-1,2,4-TRIAZOLINEDIONE-3,5-DIONE β -DICARBONYL REACTION

No.	R	R'	R''	Adducts(N)	M.P. °C	CHN Analysis	
						Calcd.	Found
35	p-tolyl	CH ₃	CH ₃	1:1(1)	190-2	58.13; 5.19; 14.53	57.76; 5.24; 14.30
34	p-tolyl	CH ₃	OC ₂ H ₅	2:1(2)	228-31	56.69; 4.72; 16.54	56.75; 4.78; 16.57
32	phenyl	CH ₃	OC ₂ H ₅	1:1(1)	153-4	55.08; 4.92; 13.77	55.65; 4.94; 13.82
33	phenyl	CH ₃	OC ₂ H ₅	2:1(2)	199-202	55.00; 4.17; 17.45	54.65; 4.34; 17.12
26	phenyl	CH ₃	CH ₃	1:1(1)	171-3	56.72; 4.73; 15.23	56.42; 4.97; 14.90
24	phenyl	CH ₃	CH ₃	2:1(2)	215 dec	56.00; 4.00; 18.67	56.08; 4.11; 18.74
37	phenyl	φ	φ	1:1(1)	189-91	69.18; 4.26; 10.53	69.40; 4.36; 10.64
38	phenyl	φ	φ	2:1(2)	160 dec	64.81; 3.83; 14.63	64.72; 4.13; 14.42
39	methyl	φ	φ	1:1(1)	170-2*	64.00; 4.45; 12.46	63.65; 4.90; 13.01

TABLE V (Continued)

No.	R	R'	R''	Adducts(N)	M.P. °C	CHN Analysis	
						Calcd.	Found
40	methyl	ϕ	ϕ	2:1(2)	164-6*	51.85; 4.52; 17.20	51.99; 4.51; 16.88
29	phenyl	ϕ	ϕ	1:1(1)	211 dec	58.54; 4.52; 14.63	58.57; 4.54; 14.57
30	phenyl	ϕ	ϕ	2:1(2)	180 dec*	55.00; 4.16; 17.50	54.89; 4.19; 17.40
41	phenyl	ϕ	ϕ	2:1(2)	218 dec	58.75; 4.49; 17.14	59.02; 4.55; 17.40

solvent, the 2:1 adduct is expected to be greatly favored if the 1:1 adduct shows significantly increased enolization relative to the pure β -diketoester. As this was suspected to be the case after obtaining 2:1 adduct under the above conditions, the 1:1 adduct, 32, was synthesized for spectral study. 0.0057 Moles of PhTD was mixed with a six-fold excess (0.034 moles) of ethylacetoacetate in methylene chloride. Reaction was complete in five minutes. On solvent evaporation, crystals dropped out of the hot solution. These were washed with cold ethyl acetate and dried overnight in a vacuum oven at 40°C. The pure white crystals melted at 152-154°C. NMR (Figure 2) of this compound in CDCl_3 shows it to exist to the extent of 90% in the enolized form. The composition of the equilibrium mixture is determined by integration of the NMR signal for the keto form as observed in the presence of mixed ethyl multiplets and methyl and α -hydrogen absorptions at 2.4 and 5.6 δ , respectively.

Adducts of 1,3-cyclohexanedione and PhTD

Reaction of 0.0057 moles of PhTD with 0.0029 moles of 1,3-cyclohexanedione in 150 ml dry methylene chloride gave complete reaction in four hours. Crystals which dropped from this solution were washed with cold methylene chloride and dried overnight in a vacuum oven at 40°C. Analysis of this product indicated it to be the 1:1 hydrated 2:1 adduct, 30. Attempts to remove this water of hydration by vacuum drying at 130°C and 0.05 mm Hg resulted in decomposition of the product. NMR gives a sharp singlet at 380 cps which slowly

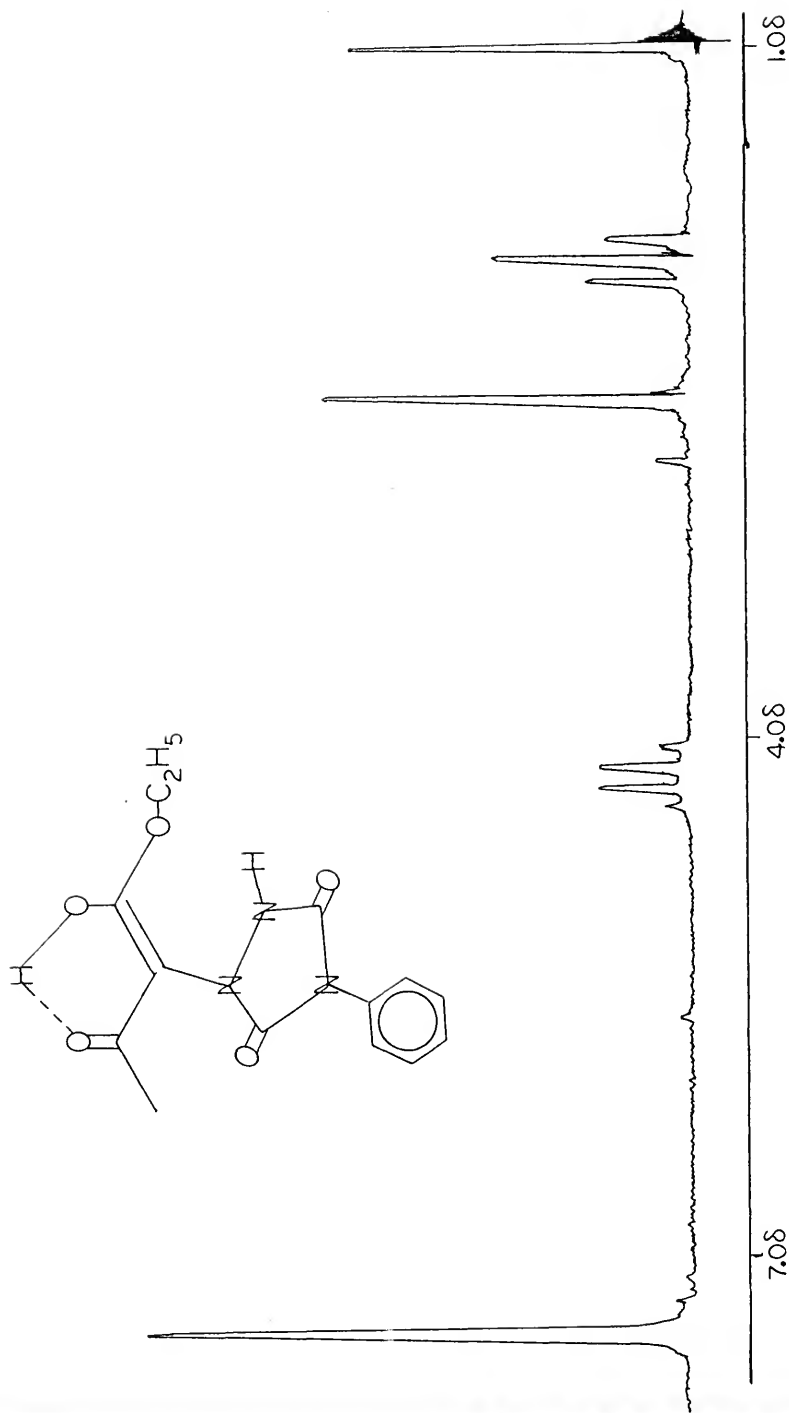
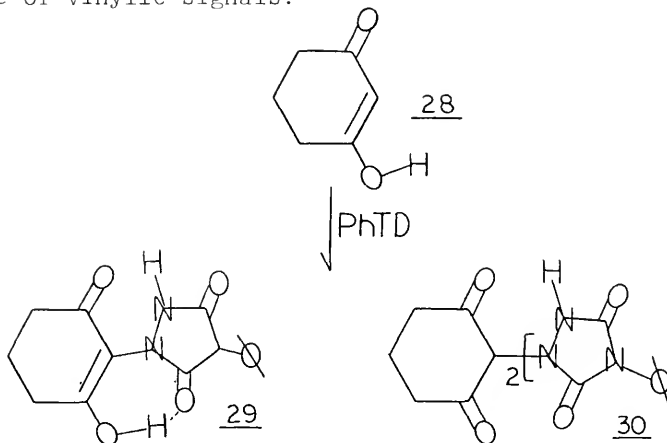


FIGURE 2. Nuclear Magnetic Resonance Spectrum of Ethyl-2-(2-hydroxy-4-phenyl-1,2,4-triazoline-3,5,5-dionyl)-3-one-butylate, 33.

exchanges with D_2O and is unique to this 2:1 adduct. On the basis of a model study, this singlet was assigned as an absorption due to a strongly hydrogen bonded amide proton.

Reaction between 0.0025 moles of PhTD and 0.025 moles of 1,3-cyclohexanedione resulted in immediate formation of the 1:1 adduct, 29, which was recrystallized from chloroform in low yields. This compound gave the expected 100% enolization in $DMSO-d_6$ as evidenced by a broad signal at 12.5 δ and absence of vinylic signals.



Adducts of dibenzoylmethane and PhTD

The 1:1 adduct of this β -diketone with PhTD was obtained by reaction of a five-fold excess of the β -diketone with PhTD in THF. Reaction was instantaneous under these conditions. Isolation of this adduct proved difficult. The 2:1 adduct, 38, was obtained by reaction of a 2:1 molar quantity PhTD and β -diketone. As with the 1:1 adduct this compound was difficult to isolate. This system proved to be somewhat different from the others studied. Although dibenzoyl methane is

essentially 100% enolized in less polar solvents, the 1:1 adduct, 37, which in previous cases demonstrated an increase in enol content at equilibrium, appeared in this case to result in decreased enolization. A sharp singlet in the up-field portion of the aromatic region (7.2 δ) which did not appear in the 2:1 adduct was suspected of being the α -proton of the keto form (Figure 3).

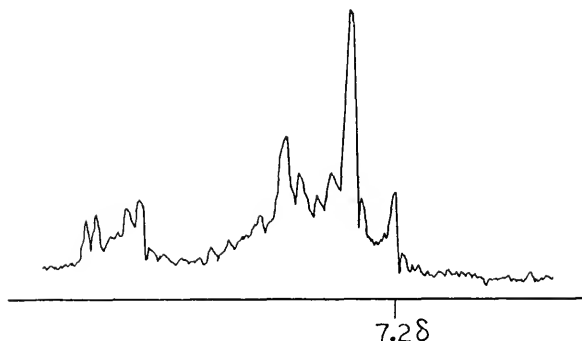


FIGURE 3. Aromatic Region Nuclear Magnetic Resonance of 2-(2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione

In an attempt to clarify the spectra in this region, and determine the extent of keto form, 4-methyl-1,2,4-triazoline-3,5-dione (MeTD) was employed in formation of the adducts. The 7.2 δ signal with this 1:1 adduct, 39, clearly separated from the aromatic signals, disappeared on addition of D_2O (Figure 4). This signal integrates to 60% of one proton in $DMSO-d_6$. The decreased enolization was supported by a model study which shows a great deal of steric problems with formation of the chelated conformation of this 1:1 adduct, and that with PhTD, which explains the reluctance observed toward

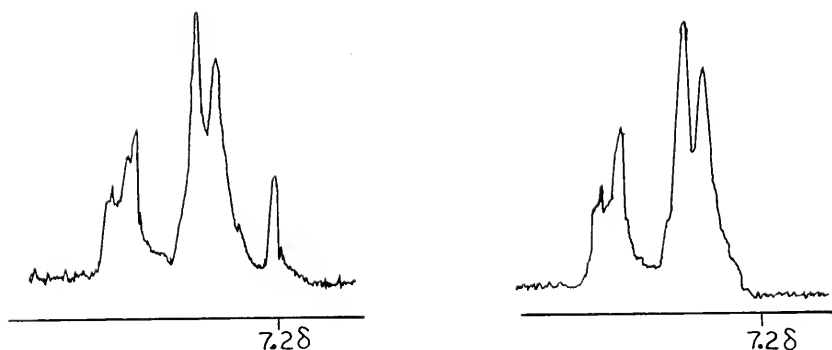


FIGURE 4. Aromatic Region Nuclear Magnetic Resonance of 2-(2-hydro-4-methyl-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione.

formation of 38 and 40.

E. Spectral Data for the Adducts of β -Dicarbonyls and PhTD, MeTD.

A summary of proton chemical shifts of the α -substituted adducts of the β -diketocarbonyl compounds studied are listed in Table VI. The methyl signals of the 1,2-pentanedione and ethylacetoacetate adducts show a pronounced upfield shift to 123-125 cps in DMSO- d_6 for the 1:1 adducts while the methyl signals of the 2:1 adducts appear at 140-143 cps. These shifts are compatible with the known methyl shift for the enol and keto forms of the pure β -dicarbonyls in this and other solvents. The chelated enolic proton for the 1:1 adducts with 2,4-pentanedione were found at 980 cps in $CHCl_3$

TABLE VI
NMR SPECTRA OF α -SUBSTITUTED β -DICARBONYLS

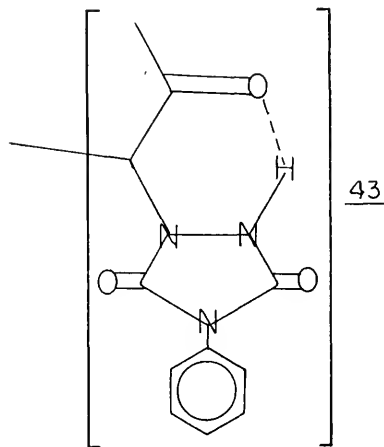
COMPOUND	R ²	R ¹ 2	R ¹ 2	R ¹ 2	OH	α H	SOLVENT
35	7.31s; 2.4s (CH ₃)	2.15s	2.15s	15.83 s-b	--	--	DMSO-d ₆
34	7.22s; 2.32s (CH ₃)	2.37s	1.3t; 4.35q	--	--	--	CDCl ₃
32	7.45s	2.42s; 2.08s	4.23 mixed quartet 1.28 mixed triplet	9.95s	5.61s	--	CDCl ₃
33	7.42	2.47s (CH ₃)	1.35t; 4.47q	--	--	--	CDCl ₃
36	7.45s	2.10s	2.10s	15.83 s-b	--	--	CDCl ₃
24	7.45m	2.35s	2.35s	--	--	--	DMSO-d ₆
37	7.44s	8.09m; 7.52m	8.09m; 7.52m	(1)	7.29s	--	DMSO-d ₆
38	7.45s	8.20m; 7.40m	8.20m; 7.40m	--	--	--	Ac-d ₆
39	2.93	8.09m; 7.52m	8.09m; 7.52m	(1)	7.16	--	DMSO-d ₆
40	2.98s	8.03m; 7.58m	8.03m; 7.58m	--	--	--	DMSO-d ₆
29	7.35s	2.45t; 1.85m	2.45t; 1.85m	12.77 s-b	--	--	DMSO-d ₆
30	7.45s	2.95t; 2.30m	2.95t; 2.30m	--	--	--	Ac-d ₆
41	7.45s	1.10s; 3.00s	1.10s; 3.00s	--	--	--	DMSO-d ₆

¹ % not sufficient for detection.

² See structure given in Table V

while those for ethylacetoacetate and 1,3-cyclohexane dione were found further upfield at 12.3 and 12.5 δ respectively.

Data from UV and IR spectra are given in Table VII. All 1:1 adducts show strong absorption in the 1580-1560 cm^{-1} region (KBr) which is attributed to the C=O stretching vibration strongly perturbed by hydrogen bonding and superimposed with the C=C stretching vibration. The 2:1 adducts all show a strong amide band at 3300 cm^{-1} . A model study indicates that this adduct may form a 6-membered hydrogen bonded conformer 43, which would be expected to prevent the amide proton from undergoing tautomerization with the 3-one of the urazole ring as it is known to do.



UV shows in each of the 1:1 adducts the appearance of an absorption in acetonitrile which is not found in the spectra of the 2:1 adducts. This band was most obvious in the case of the 1:1 adduct of 2,4-pentanedione 23 (Figure 5).

TABLE VII
IR AND UV SPECTRA OF α -SUBSTITUTED β -DICARBONYLS

COMPOUND	V(N-H) ¹	IR Spectra (KBr)		UV Spectra (CH ₃ CN)	
		V(C=O)	V(C=C)		λ , nm(log ϵ)
35	---	1700	1600	272 (3.591)	
34	3320s	1712s	---	238	
32	---	1700s	1660s	233, 250, sh (3.66)	
33	3320s	1710s	---	238	
26	---	1700s	1630	272 (3.602)	
24	3200s	1710s	---	---	
37	3170	1690s	1570	260 (4.188), 235 (3.916)	
38	3280	1680	---	263 (4.395)	
39	3200	1680	1580	313 (3.503), 251 (μ .309)	
40	3200	1680	---	359 (4.187)	
29	3250s	1690s	---	269 (3.667), 244 (4.0), 226 (4.048)	
30	3100 3250 3360	1650s	1560s	270 (2.861), 226 (4.066)	

s = strong, w = weak

¹ These bands were not distinct on some adducts. 2-Urazole absorbs at \sim 225 nm.

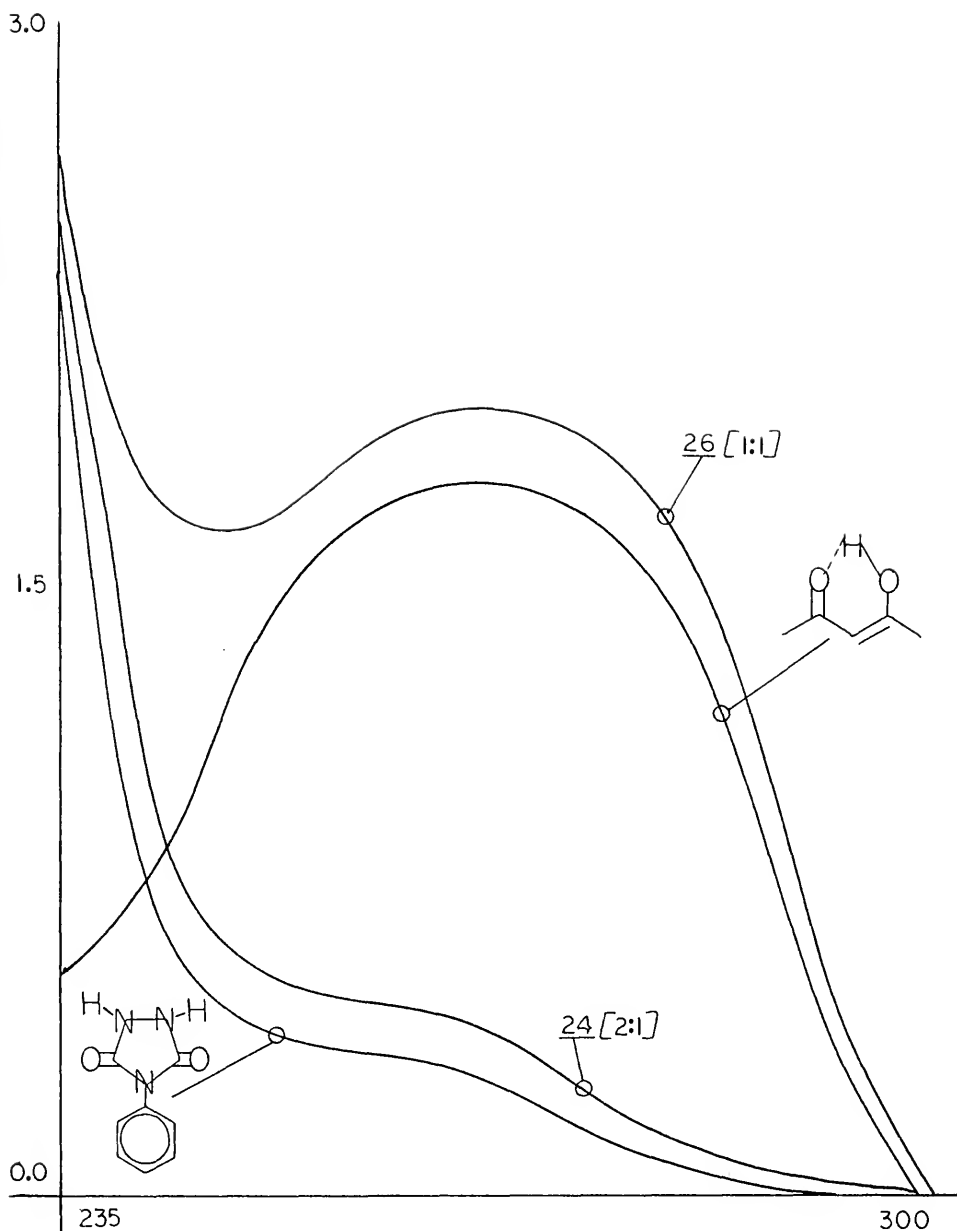


FIGURE 5. UV: Adducts 24 and 36; 2,4-Pentanedione; 4-Phenyl-urazole.

F. Copolymerization of the β -Dicarbonyl Compounds with 4,4'-(4,4'-Diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione.

All β -dicarbonyl compounds studied in this work were shown to be bifunctional. It appeared reasonable to assume that they could be copolymerized with a bis-triazolinedione, such as 16. Equimolar quantities of the dicarbonyls and PhTD at room temperature resulted in spontaneous reaction. NMR of the obtained products shows broadened peaks indicative of polymerization (Figure 6). In the case of 2,4-pentanedione two broadened signals appear in the methyl region, the lesser of the two being upfield at 120 cps. This upfield signal signifies end groups in the enolized form and therefore implies low molecular weight polymer. The viscosities of the four polymers (Table VIII) support this evidence. The major drawback of this type of polymerization reaction is the fact that molecular weights at low conversions are inherently low. These reactions can be classified as step growth addition polymerization, thus molecular weights are governed by the carothers equation:

$$\overline{DP} = \frac{1}{1 - p}$$

DP = degree of polymerization

p = conversion

The average degree of polymerization, \overline{DP} , is a function of the reaction conversion, p, and a conversion of 98% or better is necessary for high molecular weight polymers. Stoichiometric equivalence of functional groups is also a \overline{DP} controlling factor and very likely in this polymerization due to the

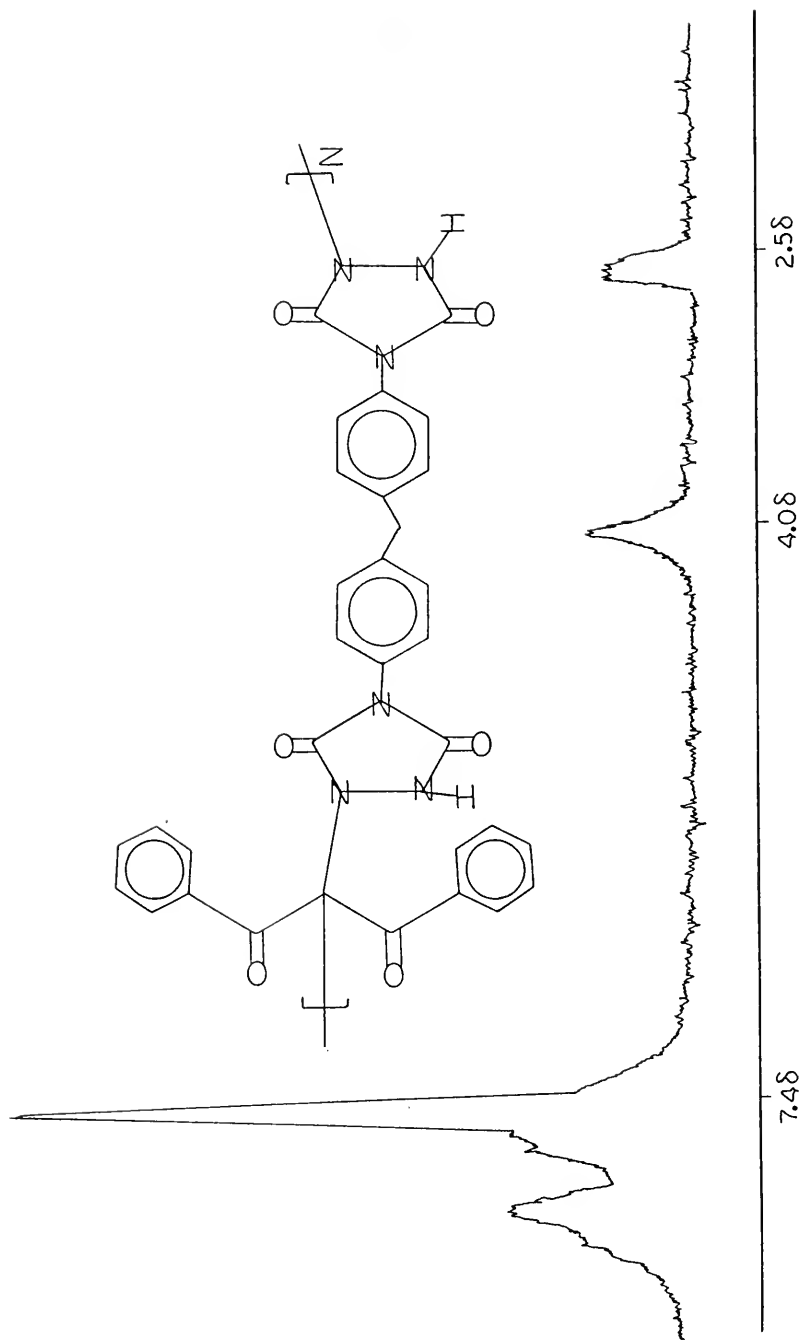
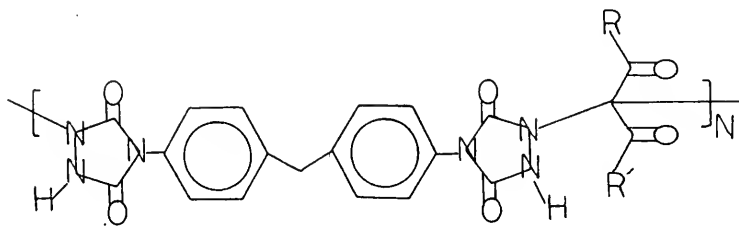


FIGURE 6. Nuclear Magnetic Spectrum of Copolymer of 16 and Dibenzolymethane

high reactivity of the triazoline moiety allowing facile side reaction with possible impurities present in the reaction. These requirements, along with the existence of a sterically hindered second addition to the α -position of the β -dicarbonyl, leads to the observed prediction of low molecular weight polymerization. All polymers when initially obtained were pale orange in color implying some N=N end groups. This color disappeared in time with exposure to air.

TABLE VIII

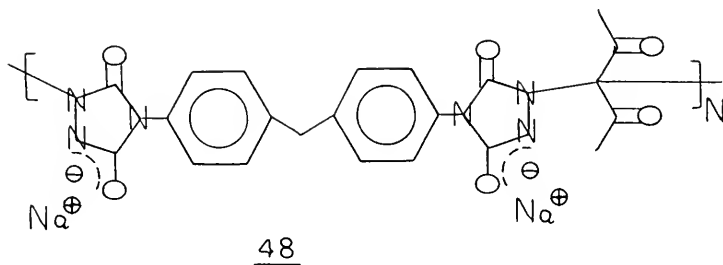
Copolymers of the β -dicarbonyls with 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione



COMPOUND	R	R'	int ¹	T _s
44	CH ₃	CH ₃	0.12	227
45	OC ₂ H ₅	CH ₃	0.12	220
46	C ₆ H ₅	C ₆ H ₅	0.09	152
47	(C ₃ H ₆)		0.12	195

¹Determined in DMF

All polymers were soluble in basic solutions (0.8 N KOH used) presumably due to the acidic amide proton and to a lesser extent, the presence of enolic end groups. Although the base soluble species was not isolated, it was assumed to be the sodium amide salt, 48.



CHAPTER III

4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONE

MODIFICATION OF DIENIC POLYMERS

A. Introduction

Dienic polymers may be modified by changing the electrostatic and steric characteristics through addition of new functionality along the chain. Modifications in the physical properties resulting from chemical modification can come from one or all of four fundamental changes.⁵⁹ (1) changing the energy associated with rotation about carbon-carbon single bonds, (2) introduction of electrostatic bonding via addition of polar functionalities, (3) covalently joining two chains and (4) disturbing the ability of a relatively stereoregular polymer to crystallize by changing its temperature transition points.

The predictability of the modification process with respect to the properties of the final product rests in part with four criteria.

1) Temperature requirements.

Heat can be detrimental to a modification process as it aids in side reactions of intra and inter-molecular nature, specifically chain scission and crosslinking.

2) Flexibility

When a suitable modification reaction is determined, its ability to give specific properties is enhanced by having the ability to accomplish the desired changes without affecting the reactivity which allows its addition to the polymer backbone. For example, "R" may represent a substituent on the modifier which may be too easily changed before its addition. This can be extended to functionality on the modifier which may be changed after reaction with the polymer.

3) Obtainable degree of addition

4) Singularity of reaction

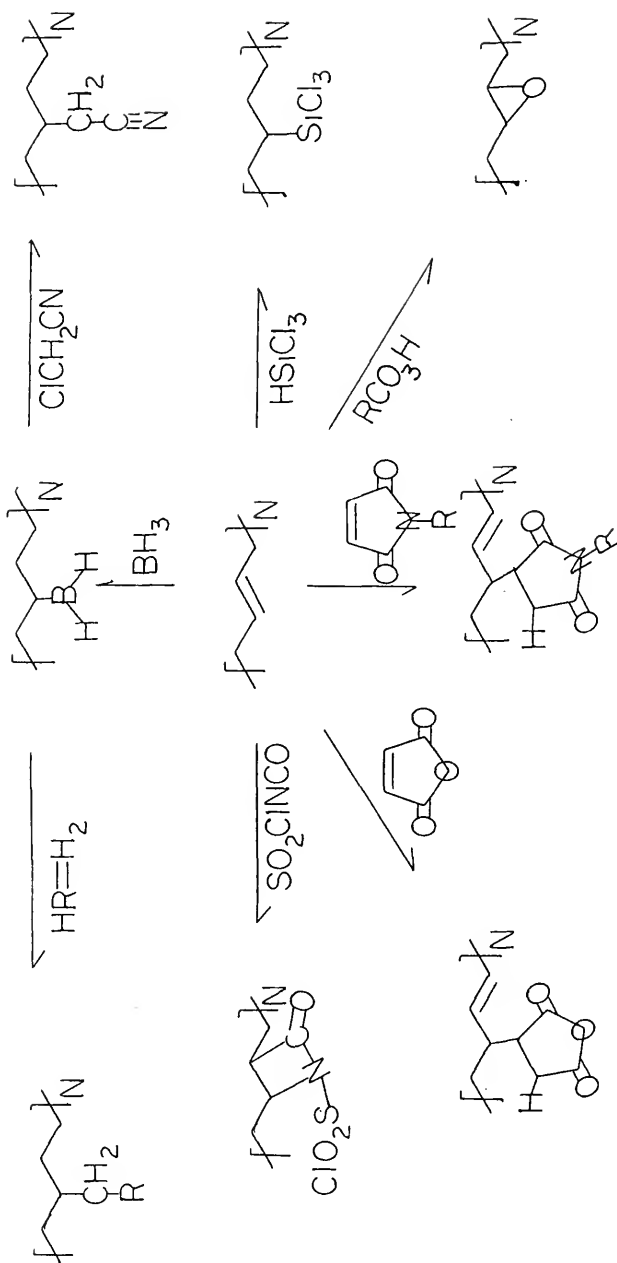
In much the same manner as depolymerization and cross-linking, modifications which are prone to more than singular addition pathways will affect the final physical properties in more than a singular manner.

Modifications accomplished to date with polydienes here summarized (Figure 7) have generally demanded somewhat adverse conditions of temperature and/or pressure and/or reactants. The ability of variation of the reaction in terms of mole modifier:mole repeating unit has also been generally limited to low ranges.

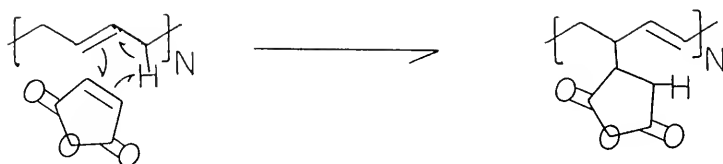
Thermal modifications

Table IX lists degrees of addition attained by various olefinic modifiers through thermal and radical means. While the radical initiated reactions are more effective at lower temperatures, they are accompanied by the unfavorable radical catalyzed side reactions such as crosslinking and chain scission.

FIGURE 7. Modifications to Dienic Polymers



The known thermal reaction, assumed to proceed via the electrocyclic "ene" mechanism results in a favorable extent of reaction of about '22' and has the desirable feature of inclusion of only the modifier in the product of the reaction.



Temperatures of up to a maximum of 240°C must, however, be employed with this reaction to obtain this extent of addition. Higher temperature which increase the extent of addition are accompanied by depolymerization.

TABLE IX
DEGREE OF ADDITION "N" OF GIVEN MODIFIERS

MONOMERS	THERMAL ¹	RADICAL
Maleic Anhydride	12	20
N-Methylmaleimide	12	22
Chloromaleic anhydride	10	--
γ -Crotonolactone	8	13
Fumaric acid	6	--
Maleic acid	5	6

continued

TABLE IX, Continued

MONOMERS	THERMAL ¹	RADICAL
p-Benzoquinone	8	--
Acrylonitrile	3	--
Tetrahydrophthalic anhydride	Very slight	

¹Reaction Temperature 240°C

Research objective:

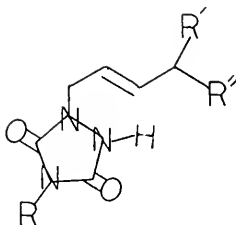
4-Phenyl-1,2,4-triazoline-3,5-dione has been shown to have 10⁴ times the reactivity of conventional olefins in its thermal reaction with allylic systems.³⁷ As a model reaction for a 4-substituted triazolinedione-ene addition to a dienic polymer, 1-butene was allowed to react with methyl and phenyl substituted triazolinediones. Although the olefin was in excess, reaction times of less than ten minutes were sufficient for complete reaction to yield the ene adducts 50 and 51 (Table X). Adducts 52 and 53 with 4-methyl-1-pentene also formed quantitatively at room temperature in less than ten minutes (Table X).

In addition to undergoing a facile 'singular' reaction with allylic systems, triazolinediones enjoy the potential for chemical modification on the 4-substituent without altering the reactive site. The number of structural variations which may be synthesized is limited only by those isocyanates which cannot tolerate the conditions which exist during the synthetic pathways used for synthesis of the

triazolinediones.

TABLE X

MODEL COMPOUNDS ISOLATED FOR POLYMER MODIFICATION STUDY



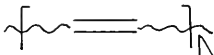
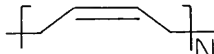
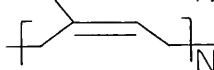
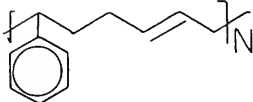

COMPOUND	R	R'	R''	MP	NMR (Ac-d ₆)		
50	CH ₃	H	H	45-6	1.7(d.3) 5.6(m.2)	3.0(s.3) 6.6 (s.1)	4.1(d.2)
51	Phenyl	H	H	126-7	1.7(d.3) 7.4(s.5)	4.1(d.2)	5.6(m.2)
52	Phenyl	CH ₃	CH ₃	115-7	0.9(d.6) 5.6(m.2)	2.2(m.1) 7.4(m.5)	4.1(d.2)
53	p-NO ₂ φ	CH ₃	CH ₃	158-0	0.9(d.6) 5.7(m.2)	2.3(m.3) 8.1(Q.4)	4.2(d.2)

These properties of the triazolinedione-ene system give "a-priori" evidence for its potential to optimize currently known modifications to dienic polymers. The purpose of this study has been to determine the reality of this assumption. Synthesis of newly substituted triazolinediones was also attempted with the purpose of widening the flexibility of the series.

B. Modification of Unsaturated Polydiene Polymers

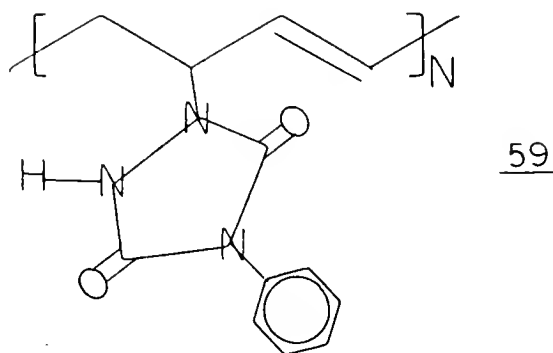
Saville⁶⁰ attempted crosslinking of natural rubber with the bis-triazolinedione, 16, in the solid state. He found the modifier to be much too reactive and reported what he called "surface reaction as opposed to homogeneous cross-linking". It seemed feasible that thermal addition of the triazolinedione moiety could be accomplished in solution resulting in uniform modification of the polymer. The system was approached in a manner which would allow its evaluation in each of the four areas listed (page 41) as criteria for modification. Due to ease of preparation and known purity, methyl, phenyl and the bis-phenyl, 16, triazolinediones were employed in the study. The polydienes were obtained from Cellomer Associates, Aldrich Chemical Co., or were synthesized in this laboratory.⁶¹

POLYDIENES FOR MODIFICATION WITH TRIAZOLINEDIONES

COMPOUND	NAME	STRUCTURE	SOURCE
54	Random Cis-Trans Butadiene		Cellomer Aldrich
55	Cis-Butadiene		Cellomer
56	Cis-Isoprene		Cellomer
57	Styrene (45%)-Butadiene		Cellomer
58	Maleic Anhydride-Furan Copolymer		This Lab ⁶¹

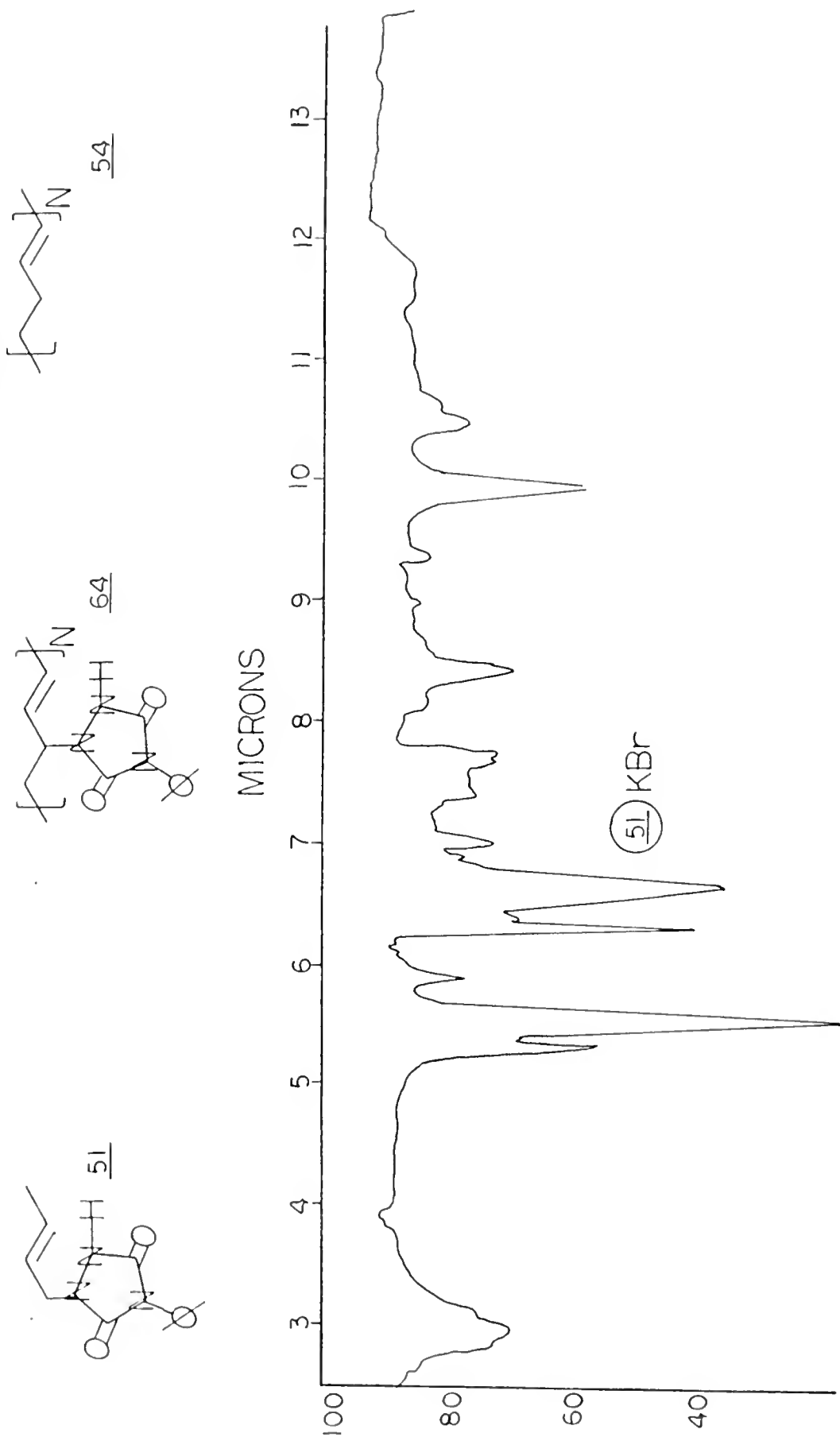
Development of modification conditions

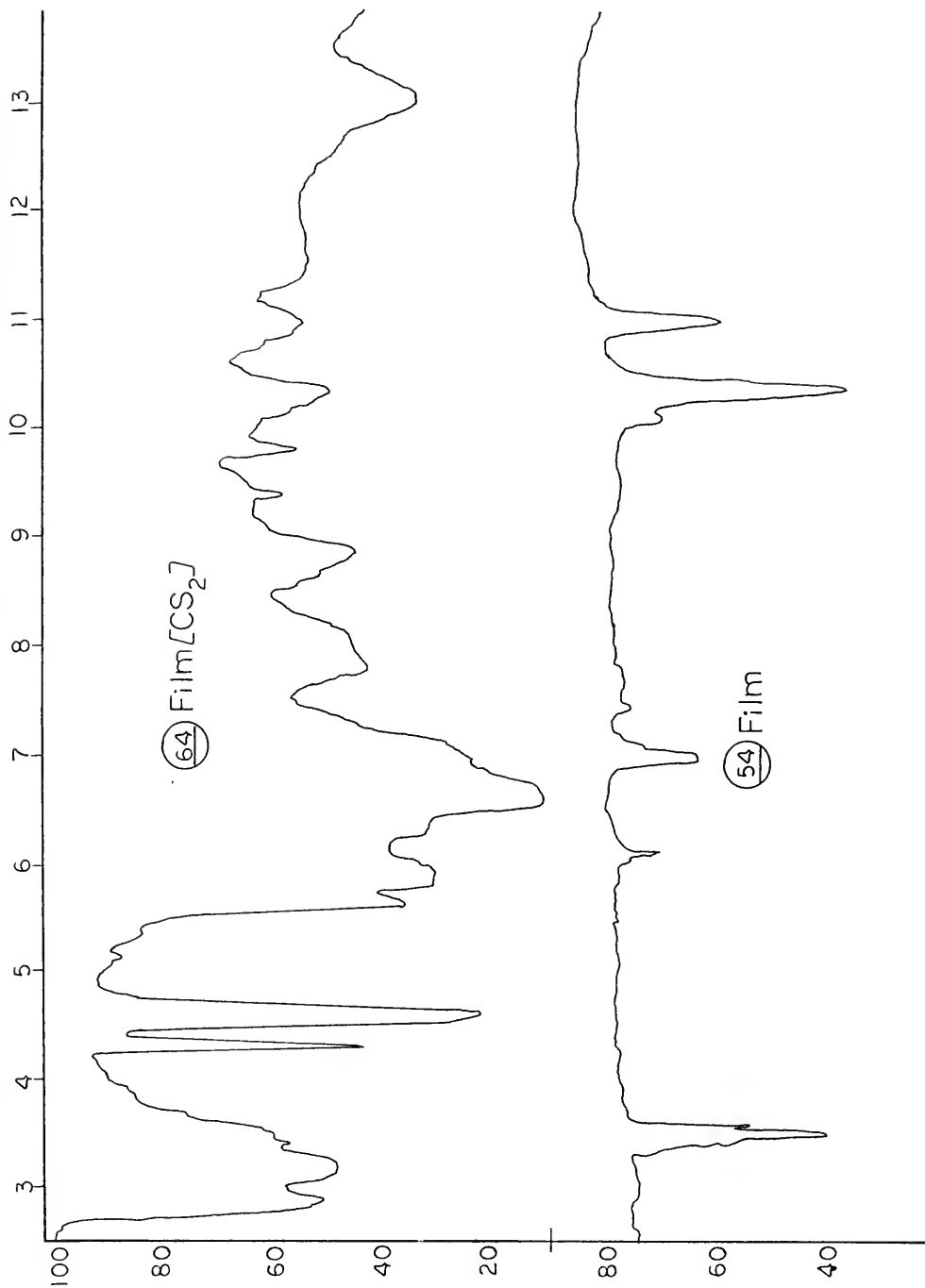
Polymer modifications were originally attempted in THF solutions. The first addition was carried out on the cis-trans polybutadiene, 54. The polymer, 0.27 grams, (0.005 moles) was added to 0.43 grams (0.0025 moles) PhTD dissolved in dry THF. A sample of pure PhTD was added to a second sample of THF as a control. The reaction was stirred for 15 hours after which the solution was completely decolorized. UV analysis on the control indicated a 10% decrease in PhTD concentration from decomposition in the solution. The modified polymer was washed with acetone after removal of the solvent and dried at 40°C and 0.5 mm Hg. The infrared spectrum of the modified polymer was found to be similar to those of the model compounds, having absorptions at 1750 and 1710 cm^{-1} characteristic of the urazole system (Figure 8) as well as strong N-H absorptions at 3500 cm^{-1} . The structure assigned is therefore that of the ene addition product, 59.



Triazolinediones are known to have a short lifetime in cyclic ethers such as THF as was shown by the UV determination on the control solution. A similar UV study indicated

FIGURE 8. Infrared Spectrum of 1-(2-Hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-2-butene, 51, PhTD Modified Random Polybutadiene, 64, and Random Polybutadiene



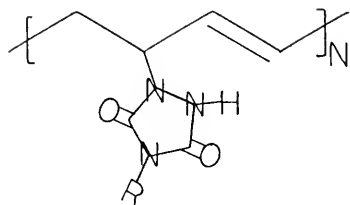


PhTD had a shelf life of several weeks in dry benzene. Initial experiments with this solvent resulted in large non-uniformly modified particles of polymer which precipitated from solution after short periods of less than one hour. Further inspection showed the original polymer solutions to contain small masses of partially dissolved polymer. All subsequent modifications were then preceded by careful filtration of the solutions through glass wool before addition of the modifier. The modified polymers in all except those cases in which addition was less than 6% were found to be insoluble in benzene and came out of solution within the first hour of reaction. The polymer, however, swelled in the solvent allowing reaction to continue long after dissolution. The modified polymers (Table XI) were easily filtered by conventional vacuum filtration through coarse sintered glass filters.

Flexibility of modification with triazolinediones

Triazolinediones may be substituted in a multitude of ways at the 4-position. This allows, in theory, all alkyl and aromatic substitutions as well as those which may be synthesized containing reactive functionality. It is reasonable to assume that the 4-substituent would affect the rate of addition of a given member of this family to polymers. A kinetic study was undertaken on a model system employing a range of substituted modifiers designed to simulate a range of electronic effects which might be encountered. The model compound, 4-methyl-1-pentene was permitted to react

TABLE XI
TRIAZOLINEDIONE MODIFICATION OF DIENIC POLYMERS



COMPOUND	COMPOUND MODIFIED	SOLVENT	R	FEED(%)	% INCORPORATION OF MODIFIER(%N)	T _S ¹
60 ³	55	THF	Phenyl	100	85(15.61)	185
61 ³	56	THF	Phenyl	100	78(13.48)	175
62 ³	57	THF	Phenyl	100	93(13.74)	195
63 ³	54	THF	Phenyl	100	92(17.03)	210
64 ³	54	Benzene	Phenyl	100	87(16.04)	210
65 ³	54	Benzene	Phenyl	75	75(15.98)	190
66 ³	54	Benzene	Phenyl	47	45(13.90)	145
67	54	Benzene	Phenyl	20	20(09.68)	49
68	54	Benzene	Phenyl	10	11(06.44)	*
69 ³	54	Benzene	Methyl	75	63(19.19)	175
70 ³	54	Benzene	Methyl	50	47(15.39)	150
71	54	Benzene	Methyl	25	23(10.55)	*

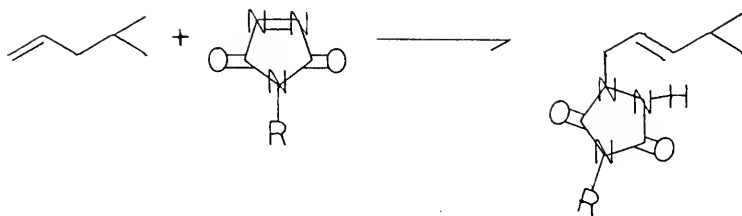
*- T_S is lower than room temperature.

¹ Rough estimate from standard Fisher-Johns MP.

² Reaction times are 48 hours at which time reaction is complete or stopped.

³ Soluble in 0.08 N KOH.

with the triazolinediones under a tenfold excess of the allylic compound to assure only 1:1 adduct formation.



All kinetic runs gave a satisfactory fit to the first order rate equation with a coefficient of correlation greater than .9995. The graphic and numerical results (Figure 9, Table XII) show that it is reasonable to assume that any modifier of this type capable of being synthesized should undergo reaction at a reasonable rate relative to that of PhTD at room temperature. Electron withdrawing substituents apparently have the effect of increasing reactivity while electron donating and aliphatic groups are reactivity decreasing. Reaction rates were also determined in two additional solvents for PhTD, THF and CHCl_3 . A small solvent effect was noted and attributed to solvation of the triazolinedione.

TABLE XII

MODEL SYSTEM KINETICS WITH SUBSTITUTED TRIAZOLINEDIONES

4-SUBSTITUENT	SOLVENT	TEMP	$K_{\text{pseudo}}^{(\text{sec}^{-1})}$	COC	ALLYLIC SYSTEM
Phenyl	CHCl_2	RT	3.08×10^{-3}	.9997	4-Me-1-pentene
Methyl	"	RT	2.47×10^{-3}	.9997	"
p-Methoxyphenyl	"	RT	2.61×10^{-3}	.9996	"
p-Nitrophenyl	"	RT	6.03×10^{-3}	.9987	"
Phenyl	THF	RT	7.00×10^{-5}	.9997	"
Phenyl	CHCl_3	RT	5.40×10^{-4}	.9997	"

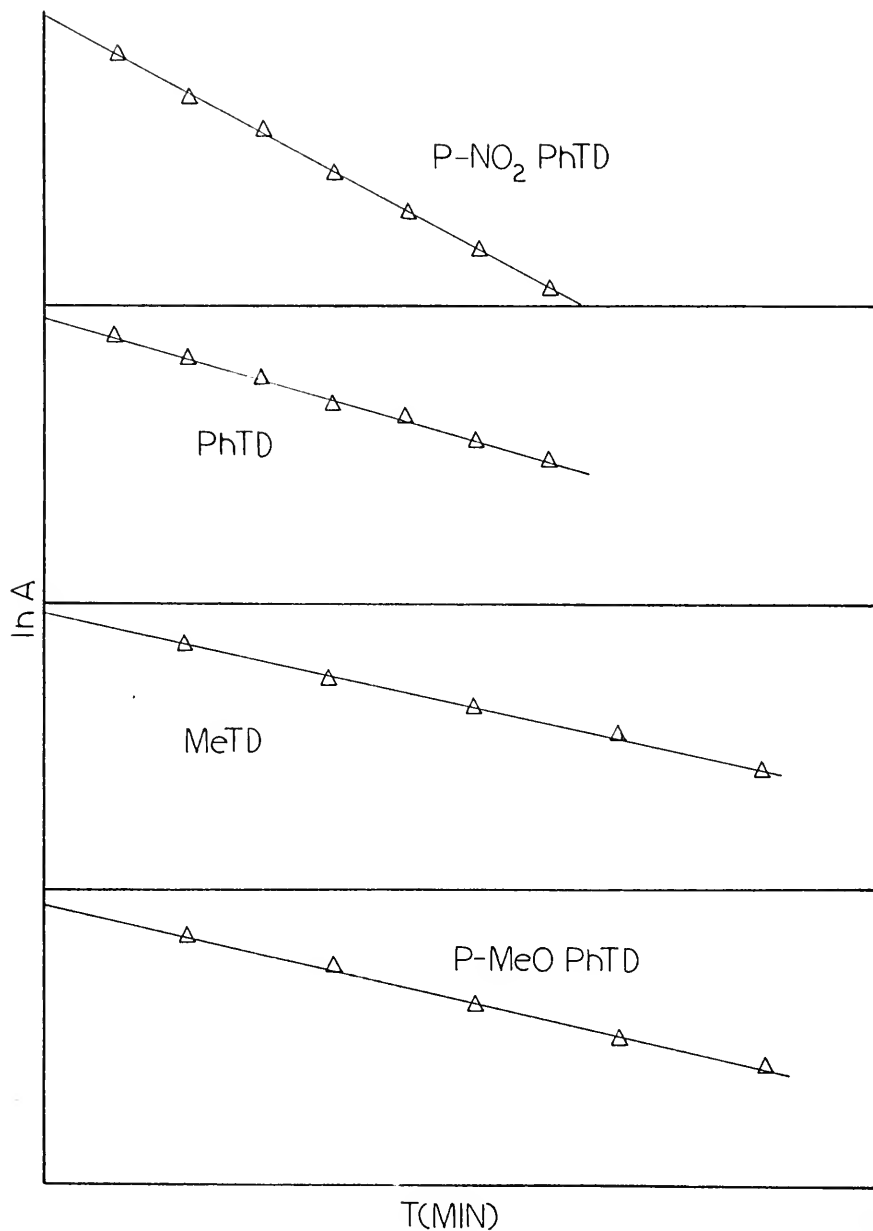
Degree of addition.

Additions were obtained ranging from 10 to 93% on a mole modifier:mole repeating unit basis as determined from nitrogen analysis of the modified polymers. Here 10% is an arbitrary beginning and 93% the maximum obtained under the reaction conditions employed in the work. As it is theoretically possible to add up to four moles modifier per repeating unit, it was assumed the low solubility of the modified polymer had much to do with the observed limit. The 100% additions attempted in THF where the polymer remained in solution during reaction gave the highest extents of addition.

Reaction singularity

Triazolinediones are known to react with allylic systems via the ene reaction. The model reactions (Table X) gave material balances indicative of complete reaction. NMR

FIGURE 9. Pseudo First Order Kinetic Plot of the Substituted Triazolidinedione:4-Methyl-1-pentene Reaction



analysis of the crude product obtained from evaporation of all solvent and unreacted olefin indicated only the presence of the expected ene adduct. Infrared of the adducts shows strong amide absorption also characteristic of the ene product. No gels were produced as all of the modified polymers completely dissolved in compatible solvents.

Reaction conditions

All modifications were carried out at room temperature. A maximum time of 48 hours was employed. The time span is believed to be the result of the modified polymer coming out of solution soon after addition begins. UV inspection shows the initial reaction to be rapid, i.e. when solution is maintained, falling off rapidly after dissolution begins.

Physical properties of the modified polymers

a) Softening points

Crude softening points of the modified polymers (Table XI) show in both the MeTD and PhTD modifications a predictable correlation between the percentage modification and change in softening points (Figure 10). Those not represented are rubbery in texture and somewhat tougher than the original polymer. The polymers of lowest percent modification demonstrate elasticity indicative of secondary crosslinking through the highly polar modifier. Those having T_g values above room temperature were white, soft fluffy powders.

b) Viscosity and gel permeation chromatography

Viscosity of the random polybutadiene taken in benzene was found to be 1.46 dl/g. The modified polymers of greater

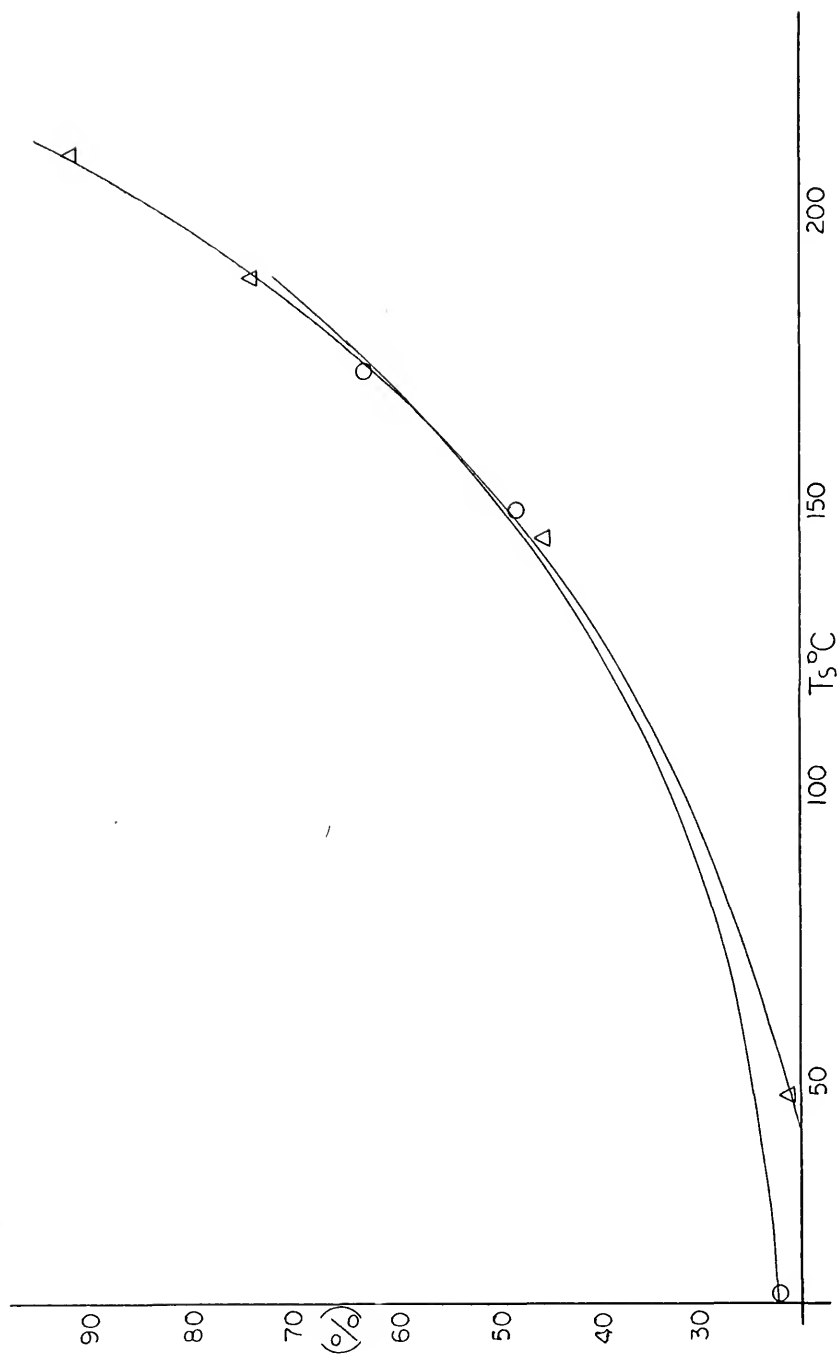


FIGURE 10. Temperature VS Percent Addition of PhTD and MeTD to Random Polybutadiene

than 80% modification were found to have greatly reduced viscosities in the range of .35 dl/g. Although vastly different solvents necessary for the viscosity study were employed, this alone is not sufficient explanation for the observed decrease. The effect is, therefore, assumed to be due to a balling up of the modified polymer due to preferential solvation of the polar urazole moiety in the viscosity solvent, 0.8 N KOH. It is also possible that the viscosity constants are drastically changed due to the dramatic increase in repeating unit weight, 380% in the case of a 90% modified chain. It seems unlikely that the other possible explanation, chain scission is taking place during modification.

Analysis of the DMF soluble modified polymers via gel permeation chromatography (Table XIII) resulted in elution counts of 12-16 in all cases corresponding to molecular size of 4×10^4 Å and Molecular weights of approximately 500,000 to 2,000,000. A somewhat arbitrary assumption is made here as GPC calibration is based on DMF analysis of monodispersed known molecular weight polystyrene. Analysis of the pure random polybutadiene, 54, resulted in an elution count somewhat higher (18) in benzene. As the modified polymer would be expected to be larger in size, the observed decrease in elution count is significant. Each of the modified samples gave what appears to be bimodal elution peaks (Figure 11). As the non-modified polymers are completely insoluble in DMF, it is unlikely that one of the peaks is due to unreacted

TABLE XIII

GPC ANALYSIS OF SELECTED MODIFIED POLYMERS¹

MODIFIED POLYMER	ELUTION COUNTS	M_w/M_n
64	12.5	1.5
	15.5	1.3
62	16.0	1.9
63	12.5	1.4
	16.0	1.6
66	12.5	1.2
	14.5	1.6
65	12.5	1.2
	15.0	2.5
69	12.0	---
	14.0	6.6

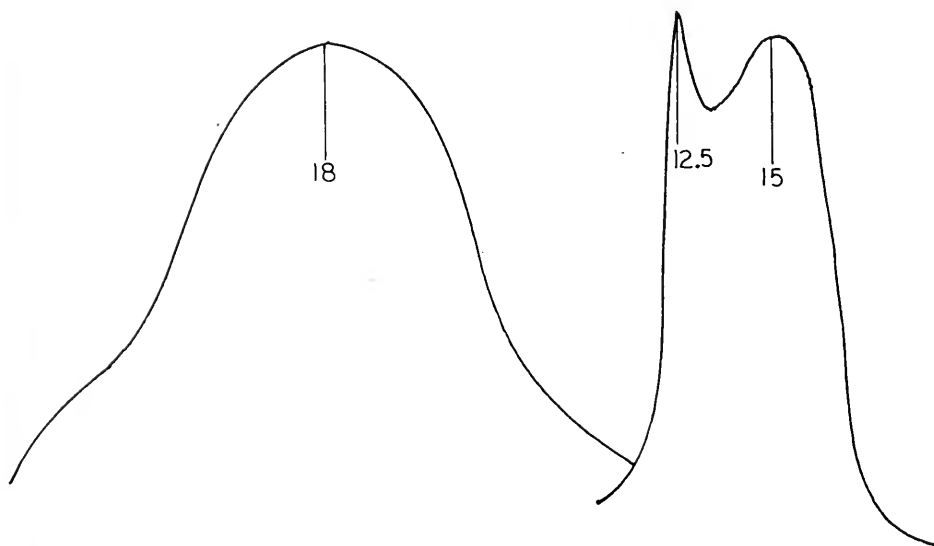
¹ In DMF.

FIGURE 11. Gel Permeation Chromatography Elution Peaks of Random Polybutadiene in Benzene and PhTD Modified Random Polybutadiene in DMF.

polymer. This is also rejected on the basis of elution counts. The random polybutadiene, 54, from Cellomer Associates was known to have $M_w = 360,000$ and $M_n = 60,000$ which is relatively polydispersed. Its GPC elution peak in benzene is broad with shoulders in the high molecular weight range (Figure 11) and appears to be close to bimodal. It is assumed, therefore, that the modification aids in separation of these components with permeation chromatography.

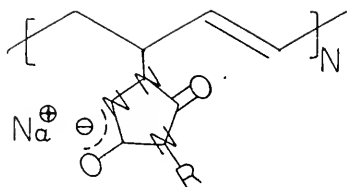
c) Solubility

Additions of greater than 45% were soluble in the following solvents when warmed.

N-methylpyrrolidone
Hexamethyl-trisphosphoramide
DMF
DMSO
Dimethylaniline

Those polymers with less modification require mixtures of solvents, one of which dissolves the original polymer. Only those polymers having the lowest additions are soluble in the original reaction medium, benzene.

All polymers with greater than 45% modification are rapidly solubilized in 0.8 M KOH and those greater than 60% modified rapidly dissolve in 1.0 M NaHCO_3 with slow evolution of CO_2 . This base solubility is attributed to formation of the resonance stabilized salt of the relatively acidic amide function. The unexpected solubility of the lower modified polymers is attributed to this resonance stabilized anion as it effectively distributes the charge over a large area.



Modifications with the bis-triazolinedione, 16.

Random cis-trans butadiene was also modified with the bis triazolinedione, 16, as well as combinations of this modifier and PhTD (Table XIV).

TABLE XIV

BIFUNCTIONAL TRIAZOLINEDIONE (16) MODIFICATION OF 54

COMPOUND	SOLVENT	MODIFIER	FEED(%)	% INCORPORATION OF MODIFIER (%N)
72	Benzene	<u>16</u>	6	---
73	"	<u>16</u>	15	---
74	"	<u>16</u>	25	21 (12.04)
75	"	<u>16</u> & PhTD	6 & 50	53 (15.06)

Room Temperature

Maximum reaction time of 8 hours.

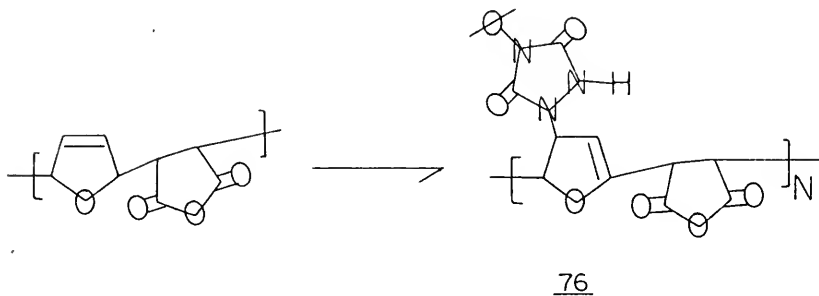
The 25% bis and 6% bis-50% PhTD modifications were gels which swell in most solvents as well as in 0.8 M KOH. The 6% and 15% bis-modified polymers were soluble in the original reaction medium, benzene, implying cyclic addition as these percentage additions of the crosslinking agent were expected

to yield gels. The possibility of unreacted $-N=N-$ ends was ruled out on the basis of the lack of colored polymer.

Reaction times were rapid relative to those observed with the PhTD additions. This increase in rate was especially obvious in the two lower additions of bis, 6% and 15%. This observation is consistent with that made with the PhTD additions as to rate of reaction with respect to precipitation of the modified polydiene.

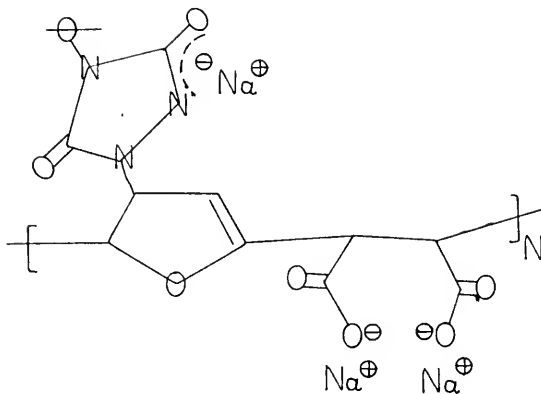
Extension to other allylic systems

PhTD was added to a previously prepared sample of low molecular weight maleic anhydride-furan copolymer in dry acetone. Somewhat longer reaction times were necessary for this system relative to that of the dienic polymers. It is possible that the ene reaction with this copolymer would be more difficult as restrictions are imposed on bond angles for the rearrangement.



NMR of the modified copolymer (Figure 10) shows new signals at 7.5 and 4.5 δ relative to the unmodified chain. The new polymer was a tan solid which softened at 155°C. The polymer

is readily solubilized in 0.5 M KOH and is expected to have greater solubility in the basic solvents due to addition of the acidic amide function.



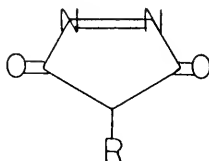
C. Synthesis of Functionalized 4-Substituted Triazolinediones.

The 4-substituted triazolinediones synthesized to date have been limited to those having aromatic or alkyl substitution. Synthesis is relatively straight forward with this series, the most difficult step being the cyclization of the alkyl substituted compounds which must be carried out with stronger bases than the hydroxide ion. Table XV lists the conventional triazolinediones synthesized for use in this work. The procedures and spectral data can be found in the experimental section. Analyses were not obtained for the oxidized urazoles as they do not possess sufficient stability to allow delivery for such.

Synthesis of 4-substituted species having reactive functional groups on the 4-substituent was attempted. The objective of

TABLE XV

4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONES



COMPOUND	R	MP ¹	PURIFICATION	COLOR ²
77*		248-50	80°/0.3mm	Light red
78*		198-00	80°/0.0mm	Light red
79*		2.6-18	85°/0.03mm	Purple
80*		268-70	pptn	Pink
16		325-30	pptn	Pink
			50°/0.1mm	Fluorescent
		204-06	70°/0.04mm	Bright red

* Synthesized for the first time in these laboratories.

¹ Melting point was found to be more accurate with the Urazole as oxidized compound decomposed slowly as it is heated.

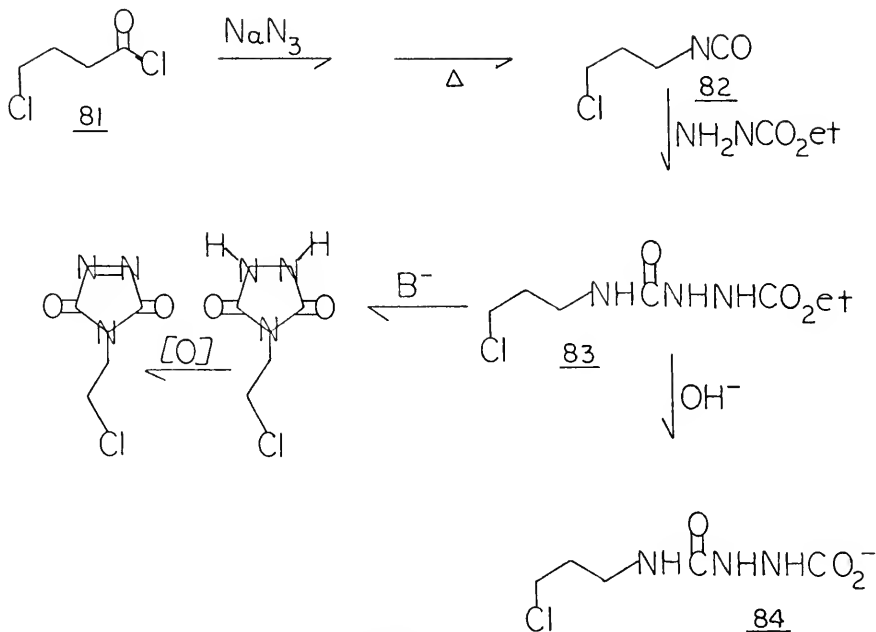
² Of oxidized compound.

this synthetic task was to obtain either labile halogen, carboxylic acid and ester or amine functionality which could undergo secondary reactions to produce ionic groups.

Attempted synthesis of 4-(γ -chloropropyl)-1,2,4-triazoline-3,5-dione.

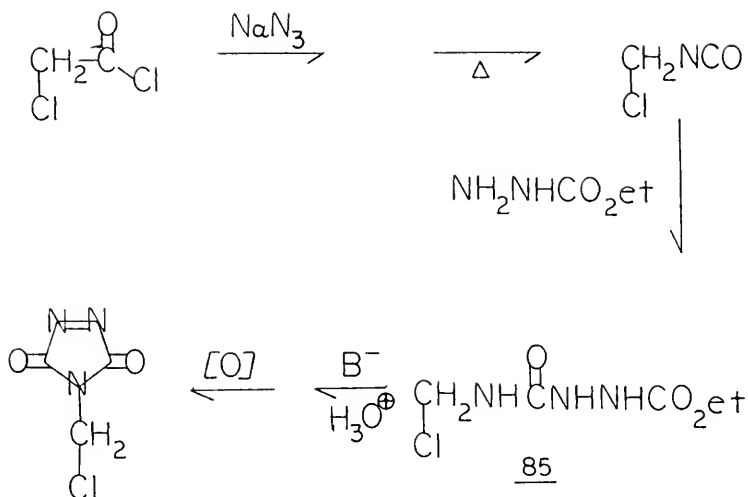
This synthesis began with preparation of γ -chloropropyl isocyanate via the Curtius method from 4-chlorobutyryl chloride, 81 (Scheme I). 33.0 grams (0.5 moles) of sodium azide were added to 150 mls of distilled water. 50 grams (.44 moles) of the acid chloride in toluene was added dropwise and the heterogeneous mixture stirred six hours. The organic layer was washed with 10% NaHCO_3 and dried with CaCl_2 overnight. Infrared of a drop of this solution on NaCl plates showed the presence of the characteristic sharp azide peak at 2100 cm^{-1} . The dried solution was heated slowly to 80°C on an oil bath to effect rearrangement to the isocyanate. Evaporation of the solvent and distillation of the resulting oil gave the desired isocyanate, 82, at 54°C , 14 mm Hg. 6.3 grams (0.052 moles) of this isocyanate was added to 5 grams (0.052 moles) ethyl carbazate in toluene at 20°C . The resulting white powder proved to be the desired γ -chloro semicarbazide, 83. Although the chloride survived this synthetic step, attempts at cyclization were not successful. Mild base cyclization attempts resulted only in formation of the carboxylic salt, 84, which on acidification decarboxylated. Attempted cyclization via sodium ethoxide in dry ethanol resulted in precipitation of sodium chloride signifying

either elimination or substitution of the chloride. Attempts at isolating these products failed. No evidence of urazole formation was found.



Attempted synthesis of 4-(chloromethyl) triazolinedione.

The methyl triazolinedione can be cyclized via hydroxide without the unfavorable quantitative formation of the unstable carbamic acid. Synthesis of chloromethyl isocyanate was attempted in hopes the semicarbazide, 85, could be prepared and cyclized with a sufficiently low $[\text{OH}^-]$ to allow the halogen to remain intact (Scheme II). Again the Curtius reaction was employed beginning with chloroacetylchloride. 44.9 grams of the acid chloride (0.39 moles) in benzene was



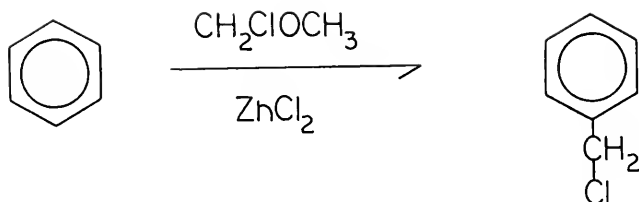
SCHEME II

added to 33.0 grams (0.50 moles) of sodium azide in water. The organic layer was separated after eight hours reaction time and dried overnight over MgSO_4 . Presence of the organic azide was shown in infrared. The rearrangement was effected by dropwise addition of the azide into benzene heated to 75°C over a period of approximately three hours. This method is preferred to that used with the γ -chloro isocyanate as the highly exothermic rearrangement was found to be much easier to control. Attempted distillation resulted in the product coming over with an approximate equimolar amount of benzene as evidenced in NMR of the distilled product. It was first assumed that the boiling point was similar to that of benzene.

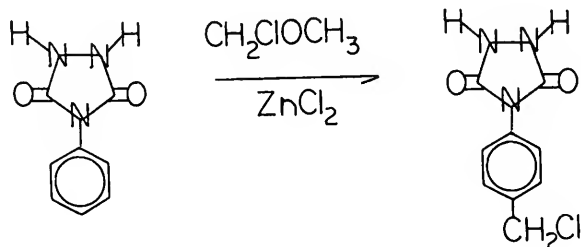
The reaction was repeated in toluene, b.p. 110°C and p-xylene, b.p. 140°C . In each case solvent distilled over with the isocyanate at a point just under the boiling point of the respective solvents. Complexing of some type with the aromatic solvent was assumed and the reaction was repeated using a synthetic octane. Separation of the azide-octane solution from the water layer resulted in two organic layers containing promising bands in the infrared $2100\text{--}2400\text{ cm}^{-1}$ range and were dried. A violent explosion resulted while these were drying and this synthesis was subsequently not attempted. An attempt was made to add ethyl carbazate directly to the benzene solution of the isocyanate assuming balanced stoichiometry from an NMR determination of the relative amounts of isocyanate and benzene. Repeated attempts to isolate pure semicarbazide, however, were not successful. NMR of the crude addition product gave broadened signals for the methyl protons and mixed multiplets for the ethyl moiety. It is possible that polymeric material was formed.

Attempted chloromethylation of 4-phenyl urazole

Non-substituted aromatic compounds may be chloromethylated employing chloromethyl-methyl ether, either neat or in solvents inert to the reactants. The conditions are mild and employ catalytic amounts of anhydrous ZnCl_2 or SnCl_2 .⁶² In a meticulously dried flask equipped with drying tube and reflux condenser, 1.0 gram (0.0057 moles) of phenyl urazole was added to 4.0 grams (0.035 moles) of chloromethyl-methyl ether and 0.1 gram of anhydrous ZnCl_2 in 10 mls of anhydrous

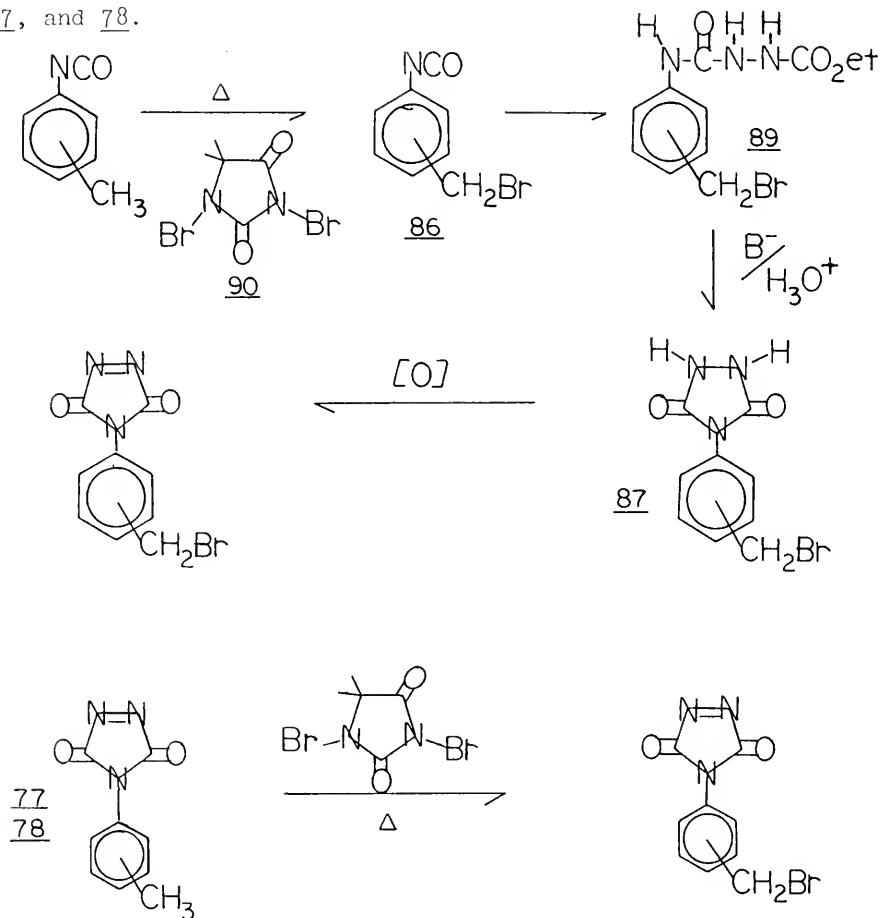


ethyl ether. After a two hour reflux period, methanol was added to the solution to destroy any unreacted chloromethyl ether. The residue obtained on evaporation of this solution was washed with H_2O to remove the inorganic salt. The solid obtained gave broadened NMR signals at 5.1 and 7.5 δ characteristic of a substituted methylated aromatic compound. The solid also gave the characteristic red triazolinedione color upon oxidation with fuming nitric acid, implying that the urazole ring integrity had been maintained. The broadened NMR signals could not be explained and attempts to obtain a pure urazole were unsuccessful. The solid dissolved in much the same manner as a polymer and is suspected of being such.



Attempted synthesis of 2-(p(m)-bromomethylphenyl)-1,2,4-triazoline-3,5-dione.

This synthesis was attempted via two routes. The first (Scheme III) involved synthesis of para (meta) bromomethylphenylisocyanate, 86, from which cyclization to the urazole, 87, was to be attempted. The second (Scheme IV) involved attempted benzylic bromination of p(m)-tolyl triazolidinediones, 77, and 78.



SCHEME IV

The bifunctional benzylic brominating agent, 1,3-dibromo-5,5-dimethylhydantoin, was employed because of its indicated ability to work effectively in the presence of other reactive functionality.⁶⁴ Para-tolylisocyanate was used as starting material. 10 grams (0.047 moles) of the isocyanate, 0.16 grams (0.00068 moles) benzoyl peroxide and 5 grams (0.018 moles) of brominating agent, 90, were added to refluxing CCl_4 and irradiated with a 500 watt tungsten lamp. A red-brown color characteristic of bromine appeared after ten minutes and disappeared after one hour. The reaction was stopped and the oil resulting from evaporation of solvent was vacuum distilled to give the desired product, 89, boiling at 115°C and 1 mm Hg. The meta-isomer was prepared giving product distilling at 108°C and 3.5 mm Hg. Previous attempts to accomplish this synthesis using equimolar quantities of bromine and isocyanate yielded products which appeared to be dibrominated, as determined by NMR integration.

9.0 grams (0.042 moles) of m-(bromomethyl) phenylisocyanate in CHCl_3 were added dropwise to 3.1 grams (0.029 moles) of ethyl carbazate cooled to -20°C . A fine white powder was obtained whose NMR (Figure 12) integrated out correctly for the desired semicarbazide. As with the bromoisocyanate, 86, this compound was successfully synthesized only after employing excess isocyanate and low temperature.

Attempts at cyclization resulted in a pale ivory solid which decomposed at 210°C and gave broadened NMR signals at 7.1 and 5.2 δ (Figure 13). This compound also appeared to

be polymeric. It gave the characteristic red color on oxidation with fuming nitric acid. Attempts at crystallization failed as would be expected with a polymeric material. It is interesting to note that the NMR spectrum in this case was identical to that from the attempted chloromethylation of phenyl urazole.

Bromination was next attempted on the m- and p-urazole, 87. NBS is known to oxidize PhTD rapidly at room temperature.¹⁸ It was correctly assumed that 90 also acts as an oxidizer for the system as mixing the two resulted in instantaneous oxidation. In order to assure precise stoichiometric control the oxidized urazole was prepared and purified by sublimation prior to the attempted bromination. The reaction conditions were identical to those employed in the bromination of the tolyl isocyanates. Reflux was established. After two hours a sample of the deep red solution was taken for NMR analysis. Evidence for bromination was found in the appearance of a sharp singlet at 4.45 δ characteristic of a bromo-substituted benzylic carbon. Samples taken at 6, 12, 18, and 24 hours indicated no further evidence of this reaction. Attempts to isolate the product by sublimation failed. It was incorrectly assumed that the free radical reaction was being deactivated through the urazole ring preventing the desired bromination. For this reason the reaction was again attempted on the m-tolyl derivative. The results were essentially the same in this case leading to abandonment of this route.

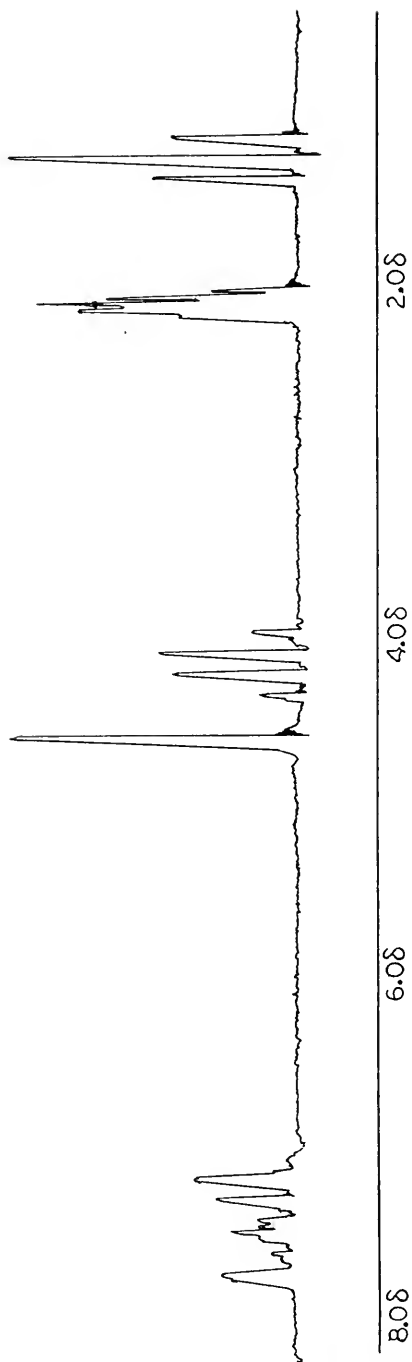
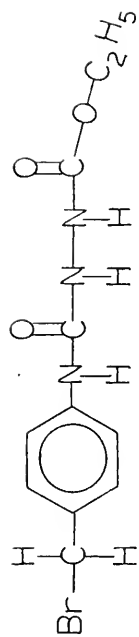


FIGURE 12. Nuclear Magnetic Spectrum of 1-Ethoxycarbonyl-4-(m-bromomethylphenyl)-semicarbazide

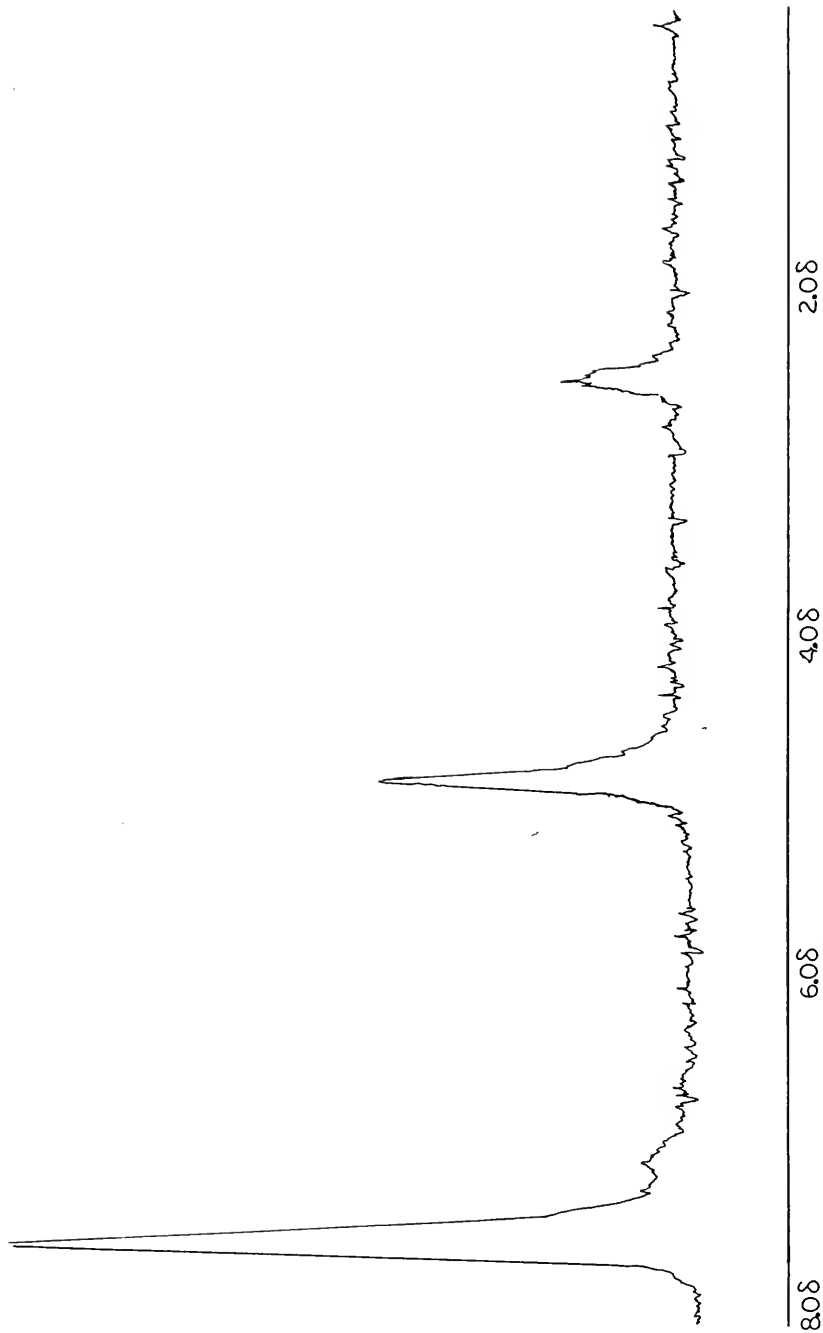
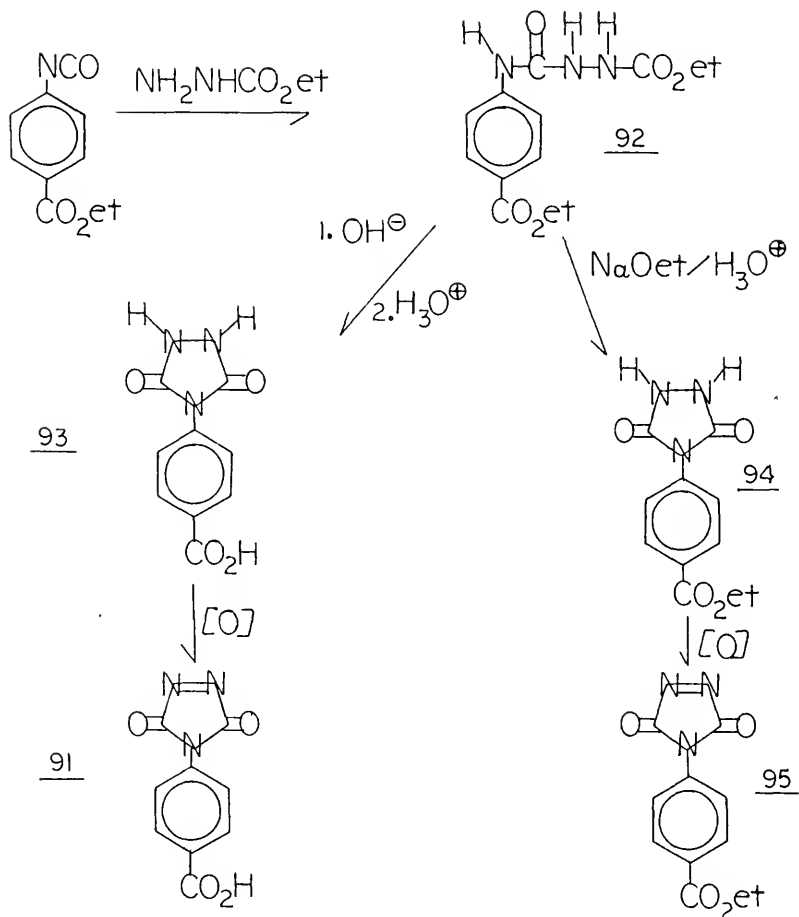


FIGURE 13. Nuclear Magnetic Spectrum of the Product of Base Cyclization of 1-Ethoxycarbonyl-4-(m-bromomethylphenyl)-semicarbazide

Synthesis of 4-(p-carboxyphenyl)-1.2.4-triazoline-3,5-dione, 96, and its ethyl ester, 95.

These compounds were prepared according to Scheme V.



SCHEME V

Upon acidification after the base cyclization of 4-carbethoxysemicarbazide, 92, the solid urazole, 93, formed in a laminar manner giving sheets of soft white solid on filtration.

Although NMR, MS analyses and melting point determination indicated a pure compound, elemental analysis indicated the compound to be the 1:1 hydrate of 93. This water of hydration was successfully removed by drying at 195°C and 0.1 mm Hg.

CHN ANALYSIS FOR 93

CALCULATED ¹	FOUND	CALCULATED ²	FOUND
45.18	45.18	48.87	48.87
3.75	3.82	3.16	2.84
17.57	17.48	19.00	18.92

1-1:1 hydrated compound.

2-After 24 hours drying at 195°C/.01 mm Hg.

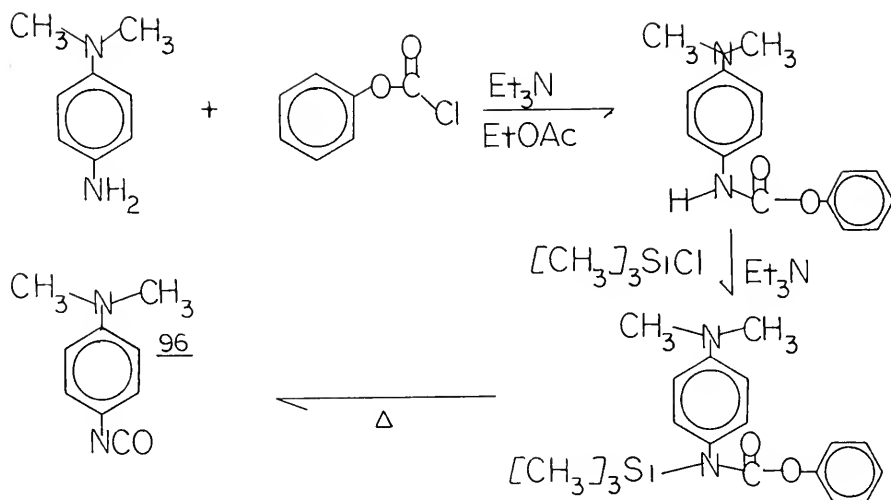
The p-carbethoxy urazole, 94, was originally prepared by esterification of 93. The reaction was carried out using a Dean and Stark reflux apparatus with ethanol-benzene and a catalytic amount of H_2SO_4 . A pale white solid melting at 198°C was obtained after isolation. This method was employed to test the feasibility of esterification of the carboxylic acid-substituted urazole as a potential modification step after introduction of the carboxylic acid-substituted triazolinedione, 91, into the substrate. A better method for preparation of the p-ester was found in the sodium ethoxide cyclization of the carbethoxy semicarbazide, 92. Addition of the semicarbazide to a 1.4 molar excess of a sodium ethoxide-ethanol solution resulted in a pale yellow solution after six hours refluxing. The orange pink precipitate

obtained from addition of the solution to hexane was rapidly solubilized in water and gave the characteristic triazoline-dione color on oxidation with HNO_3 . This salt was acidified gently at 10°C in an ethanol solution causing precipitation of NaCl . The filtered, evaporated solution gave a powder which was recrystallized from ethanol-water to give the tan solid 95.

Initial attempts to obtain the oxidized urazoles, 91 and 95, gave oils on evaporation of the CH_2Cl_2 solutions of oxidized material. This red oil, in each case, rapidly decomposed on exposure to air. As the polarities of the desired compounds are greatly increased relative to those previously prepared, it was assumed that excess oxidizing agent was being absorbed onto the compound. Subsequent attempts to isolate the compounds included washing the oxidized CH_2Cl_2 solution with 2-3 portions of water and drying over MgSO_4 before evaporation of the solvent. This method gave low yields of the desired products.

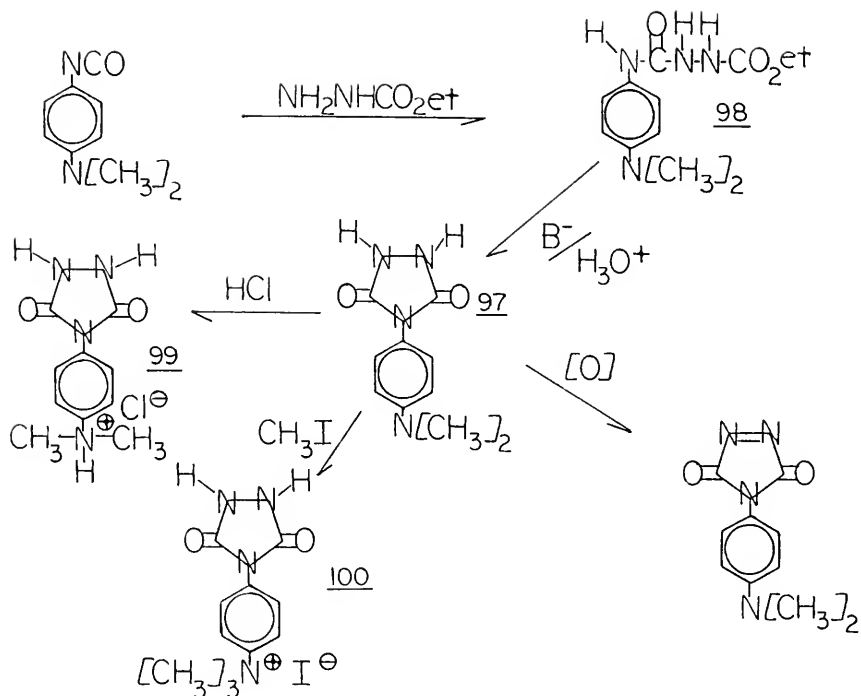
Synthesis of 4-(p-N,N-dimethylaminophenyl)-1,2,4-triazoline-3,5-dione and related salts.

This synthesis began with the novel synthesis of p-N,N-dimethyl-p-phenylenediamine isocyanate, 96, instituted by Gerber and Kricheldorf.⁶³ The corresponding urazole, 97, was then prepared in a straight forward manner as before (Scheme VI). Acidification after base cyclization of the semicarbacide, 98, resulted in protonation of the tertiary amine allowing dissolution. Careful pH control was necessary



to precipitate the amine. Both the HCl salt, 99, and methyl iodide salt, 100, were prepared with ease by HCl acidification of an acetone solution and refluxing with CH_3I , respectively. Both salts were readily soluble in water and both were isolated as hydrated salts as determined from NMR and elemental analyses. Attempts to remove the water of hydration failed.

Oxidation of the aminourazole was carried out by a new method employed in the preparation of PhTD discovered by Moore, Muth and Sorace.¹⁹ This method provides a semi-quantitative 'in situ' oxidation of phenyl urazole to PhTD in dry DMSO as determined by UV. Similar results were observed with the aminourazole, 97. The previously used methods of urazole oxidation were ineffective with this compound. DMSO employed in the oxidation was dried over CaH_2 and distilled



SCHEME VI

prior to the oxidation. Attempts to use stock DMSO in the oxidation resulted in formation of the purple oxidized color which immediately disappeared.

Oxidation of the HCl and CH_3I salts, 99 and 100, has not been successful with any of the oxidation methods employed in this work.

CHAPTER IV

EXPERIMENTAL

A. Equipment and Data

All temperatures are reported uncorrected in degrees centigrade. Nuclear magnetic resonance spectra were measured with a Varian A-60A Analytical NMR Spectrometer. All chemical shifts are relative to tetramethylsilane.

Infrared spectra were obtained with a Beckman IR-8, IR-10 and Perkin Elmer Infrared Spectrophotometer.

Melting points were determined with a Thomas Hoover melting point machine.

Mass spectra were obtained with either a Hitachi Perkin Elmer RMU Mass Spectrometer or high resolution computerized MS-30.

Elemental analyses were performed by one of the following: Galbraith Laboratories, Heterocyclic Chemical Corp., or Microlab.

Viscometry was carried out with a Cannon # 75 Viscometer.

Gel Permeation Chromatography was performed on a Waters and Associates GPC-300 with 4 series columns having pore sizes: 10^5 , 10^4 , 10^3 , 2-500 Å.

Procedure for room temperature kinetic measurements

2 ml Portions of equimolar solutions of PhTD and the

1:1 adduct of PhTD and 2,4-pentanedione were pipetted into an ultraviolet cell. The 1:1 adduct is used due to its established 100% enolization. Visible spectra at 545 (unless otherwise noted) was recorded versus time taking no less than 7 readings. The reaction was determined to be second order overall due to its fit with the second order rate expression:

$$\frac{1}{A_t} = \frac{k}{a} t + \frac{1}{A_0}$$

where A = absorbance at time "t"

a = PhTD absorbtivity times cell path length (1cm)

k = second order rate constant

A₀ = Absorbance at time zero

Pseudo first order rates were determined in a similar manner. 2 ml portions of 1:10 molar solutions of PhTD:β-di-ketone were pipetted into the UV cell. Due to the speed of the reaction between PhTD and 2,4-pentanedione in THF the kinetics were run at reduced temperature to demonstrate maintenance of the data's fit to the first order kinetic equation:

$$\ln \frac{A_t}{a} = k_t + A_0$$

The UV cell was cooled via constant temperature circulating ethylene glycol system to 6°C. Individual solutions were allowed to reach this temperature before mixing. All other runs were taken at room temperature.

The opposing 10:1 reaction could not be carried out due to the possibility of a side reaction forming the 2:1 adduct.

Results are listed in the discussion section of this work.

THF was obtained in high purity for kinetic runs by vacuum line distillation from the potassium salt of the dianion of benzophenone to assure freedom from peroxides.

1,1,2,2-Tetrachloroethane was purified by distillation over 3A molecular sieves through a 10" vigreux column. No further effort was made to remove possible HCl impurities.

1,4-dioxane and ethylacetate were purified by distillation over CaH_2 through a 36" vigreux column.

Kinetics of 4-substituted-1,2,4-triazoline-3,5-diones with 4-methyl-1-pentene

Pseudo first order kinetics of the substituted triazolinediones with 4-methyl-1-pentene were carried out in a manner identical to that used with PhTD and the β -diketones. 1:1 molar solutions of PhTD and 4-methyl-1-pentene were mixed at room temperature. Pseudo first order conditions were used due to the potential for more than 1:1 adduct formation. Results are listed in the discussion portion of this work.

B. Synthesis of 1,2-Dihydro-4-substituted-1,2,4-triazoline-3,5-diones (4-Substituted Urazoles)

Ethyl carbazate¹⁵

Diethyl carbonate (1.80 mol, 200.0 g) and 99% hydrazine hydrate (1.90 mol, 88.0 g) were stirred at room temperature for one half hour. Initially the two phase system reacted with mild exothermicity, and one phase resulted. The clear liquid was distilled twice at 95° and 12 mm yielding 130 g (74.2%) of a liquid which on standing solidified to a white solid, m.p. 45-47° (lit.⁴ 44-45.5°).

1-Ethoxycarbonyl-4-phenylsemicarbizide

Ethyl carbazate (0.64 mol, 62.0 g) was dissolved in 200 ml benzene and was brought to 10° in a three-necked round bottomed flask equipped with an addition funnel, a reflux condenser fitted with a drying tube, a thermometer and a mechanical stirrer. Stirring was initiated and phenyl isocyanate (0.64 mol, 59.0 g) in 100 ml benzene was added dropwise through the addition funnel keeping the temperature between 10° and 20°. As the addition proceeded, a white precipitate appeared and remained until the addition was complete. The mixture was refluxed for one half hour, resulting in solution of the precipitate. Upon cooling the precipitate reappeared and was filtered. The precipitate was washed with two 75 ml portions of cold benzene

yielding 110.2 g (91.3%) of a white solid, m.p. 151-52° (lit.⁶⁴ 154°).

4-Phenyl urazole

1-Ethoxycarbonyl-4-phenylsemicarbazide (0.55 mol, 124.0 g) was added to 300 ml hot, stirred 4M potassium hydroxide. Upon complete solution, the light yellow solution was filtered and cooled. The solution was acidified with 50% hydrochloric acid resulting in a voluminous white precipitate. The precipitate was vacuum filtered and washed several times with cold water. The filtrate was tested for additional precipitate by slowly adding 50% hydrochloric acid. Any solid that appeared was filtered, washed and combined with the original precipitate. The precipitate was dried overnight in a vacuum oven yielding 69 g (78.0%) of a white solid, m.p. 204-208° (lit.⁶² 206-7°).

Additional urazoles

The synthesis of the following urazoles was accomplished according to the method given above for 1,2-dihydro-4-phenyl-1,2,4-triazoline-3,5-dione (4-phenyl urazole). Spectral and analysis data are given here for the functionalized p-nitro-phenyl and p-methoxyphenyl urazoles.

4-(p-Tolyl) urazole

4-(m-Tolyl) urazole

4-Methyl urazole

1,2-Dihydro-4-(p-methoxyphenyl)-1,2,4-triazoline-3,5-dione,

79 (4-(p-methoxyphenyl) urazole).

Infrared absorbanices were found at (Nujol) 3200 (m, b), 2900 (s), 1760 (m), 1680 (s), 1600 (m), 1590 (w), 1500 (m), 1450 (s), 1380 (s), 1300 (m), 1240 (m), 1220 (m), 1180 (m), 1110 (m), 1090 (w), 1040 (w), 1020 (w), 1010 (w), 1000 (w), 965 (w), 930 (w), 850 (w), 840 (s), 800 (w), 785 (s), 760 (m), and 720 cm^{-1} .

NMR signals were found at (DMSO- d_6) 9.12 δ (s, broad, 2), 7.2 δ (Q, 4), 3.8 δ (s, 3).

Anal. Calcd. for $\text{C}_9\text{H}_9\text{N}_3\text{O}_3 \cdot \text{H}_2\text{O}$: C, 48.00; H, 4.88; N, 18.66. Found: C, 48.22; H, 4.78; N, 18.29.

1,2-Dihydro-4-(p-nitrophenyl)-1,2,4-triazoline-3,5-dione,

80 (4-(p-nitrophenyl)urazole).

Infrared absorbances were found at (Nujol) 3200 (m, b), 2900 (s), 1780 (w), 1600 (s), 1610 (w), 1600 (w), 1530 (m), 1500 (m), 1460 (s), 1380 (m), 1350 (w), 1300 (w), 1200 (w), 1120 (w), 1090 (w), 855 (m), 790 (m), 760 (w), 750 (w), 720 (w), and 695 (w) cm^{-1} .

NMR signals were found at (DMSO- d_6) 8.25 δ (Q, 4), 5.0 δ (s, broad, 2).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_4\text{O}_4 \cdot \text{H}_2\text{O}$: C, 38.70; H, 3.62; N, 22.5. Found: C, 38.75; H, 3.53; N, 21.91.

4,4'-(4,4'-Diphenylmethylene)-bis-1,2-dihydro-1,2,4-triazoline-3,5-dione.

A 100 ml solution of bis-(4-isocyanatophenyl)methane (0.100 mol, 24.0 g), vacuum distilled before use, was slowly added to a 200 ml solution of ethyl carbazate (0.200 mol, 19.0 g) in benzene, which was cooled to maintain the temperature at 45° or below. After the addition was complete, the mechanically stirred mixture was refluxed for one half hour to insure complete reaction. The resulting insoluble, white solid was filtered and dried after stirring overnight. The bis-semi-carbazide soon melted at 236-245° (lit.⁴⁷ 240-244°) and weighed 40.1 g (93%).

The bis-semicarbazide (0.087 mol, 40.0 g) was slowly added to a 100 ml 4N aqueous solution of potassium hydroxide and 100 ml ethanol. The mixture was heated on a steam bath for two hours followed by filtration of a small amount of insoluble solid. The light yellow filtrate was slowly added to an excess of 5% aqueous acetic acid, precipitating the bis-urazole, an off-white solid, m.p. 325° (decomposition), (lit.⁶⁵ 320°). The yield was 34.9 g (95%).

1-Ethoxycarbonyl-4-(p-carbethoxyphenyl)-semicarbazide. 92

p-Carbethoxyphenylisocyanate (25 g, .13 mol) in 100 ml dry benzene was added dropwise to a benzene solution of 12.5 g (.13 mol) ethyl carbazate in a 500 ml round bottomed flask equipped with reflux condenser, thermometer, mechanical stirrer, and 250 ml addition funnel. Addition was controlled to keep the ice cooled reaction at 15-20°C. A white precipitate

formed immediately. The reaction mixture was allowed to warm to room temperature and stirred 15 minutes after addition was completed. The solution was then filtered and allowed to air dry before placing it in a vacuum oven at 40°C. The white powder melts at 191-2°C. Infrared absorbances were found at (KBr) 3320 (b), 3220 (s), 3.50 (s), 3000 (s), 2960 (s), 2920 (s), 1700 (b), 1600 (w), 1560 (b), 1530 (b), 1510 (s), 1485 (s), 1480 (s), 1450 (w), 1410 (s), 1370 (s), 1320 (s), 1280 (b), 1230 (b), 1170 (s), 1100 (m), 1060 (w), 1020 (m), 900 (w), 860 (s), 830 (w), 765 (s), and 695 (s) cm^{-1} . NMR signals were found at (DMSO- d_6) 1.3 δ (Q, 6), 4.2 δ (m, 4), 7.7 δ (Q, 4), 8.1 δ (s, 1), 9.0 δ (s, 1), 9.2 δ (s, 1). Mass spectral molecular ion at 295 m/e.

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_5$: C, 52.88; H, 5.76; N, 14.24.
Found: C, 52.72; H, 5.80; N, 14.34.

p-Carbethoxyphenyl Urazole 94

1-Ethoxycarbonyl-4-(p-carbethoxyphenyl)-semicarbazide (92) (3 g, .01 mol) was added to 100 ml absolute ethanol containing .32 g (.014 mol) reacted sodium in a dried 250 ml flask with condenser and magnetic stirring. The initial color of the solution was yellow. This quickly became a deep orange. After 6 hours reflux the solution was again a pale yellow and slightly turbid. The cooled mixture was added dropwise to hexane yielding a fine pink solid. This was then dissolved in 50 ml ethanol (abs) and acidified resulting in precipitation of NaCl. The filtered solution was reduced in volume. A white solid formed having a m.p. of 199-201°C.

Infrared absorbances were found at (Nujol) 3200 (m), 2900 (s), 1780 (w), 1725 (s), 1685 (s), 1610 (w), 1520 (w), 1460 (s), 1420 (w), 1380 (m), 1310 (w), 1280 (m), 1190 (w), 1120 (m), 1040 (w), 855 (w), 790 (w), 770 (w), and 695 (w) cm^{-1} . Mass spectral molecular ion at 249 m/e. NMR signals were found at (DMSO-d_6) 10.6 δ (s, broad, 2), 7.9 δ (Q, 4), 4.4 δ (Q, 2), and 1.4 δ (T, 3).

Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_4$: C, 53.01; H, 4.42; N, 16.87. Found: C, 53.12; H, 4.45; N, 16.80.

p-Carboxyphenyl urazole 93

p-Carbethoxysemicarbazide 92 (5 g) was added to 200 ml 4M KOH. The mixture was heated with magnetic stirring on a hot plate to facilitate reaction. After solution was obtained, the system was heated for an additional 15 minutes, cooled and any insoluble material filtered off. The beaker was placed in an ice bath and acidified with conc. HCl maintaining temperature at $<20^\circ\text{C}$. After one hour, white layered flakes fell from the solution, m.p. 300° . Analysis shows this to be hydrated. Calculated for $\text{C}_9\text{H}_7\text{N}_3\text{O}_4 \cdot \text{H}_2\text{O}$: C, 45.18; H, 3.76; N, 17.57. Found: C, 45.18; H, 3.82; N, 17.48. The compound was placed in a drying pistol with ethylene glycol as reflux solvent ($195^\circ\text{C}/0.05 \text{ mm Hg}$) for 24 hours. The dried compound was more powder like. Infrared absorbances were found at (KBr): 3340 (b), 3200 (b), 1790 (s), 1700 (b), 1610 (s), 1590 (w), 1515 (s), 1450 (w), 1420 (s), 1350 (w), 1310 (w), 1270 (w), 1245 (s), 1180 (w), 1120 (s), 1015 (w), 850 (w), 790 (s), 770 (s), 730 (s), and 700 (s) cm^{-1} . NMR

(DMSO- d_6) signals were found at 7.9 δ (Q). Mass spectral molecular ion at 221 m/e.

Anal. Calcd. for $C_9H_7N_3O_4$: C, 48.87; H, 3.16; N, 19.00. Found: C, 48.87; H, 2.87; N, 18.92.

p-N,N-dimethylaminophenyl isocyanate

Phenyl chloroformate (50.0 g, 0.32 mol) was added dropwise to a solution of 600 ml dry ethyl acetate (3A molecular sieves) containing 43 grams (6.31 mol) of freshly distilled N,N-dimethyl-p-phenylenediamine (112°C/1.0 mm Hg) and 54.0 g (0.53 mol) triethylamine over a period of 30 minutes at 8°C. The mixture was stirred mechanically for two hours at room temperature after which all precipitated triethylamine hydrochloride was filtered and washed with more ethyl acetate. The solvent was removed by rotory evaporation yielding a solid which when recrystallized from absolute ethanol melted at 157-9° (lit.⁶⁶ 155-8).

A mixture of phenyl-N-(p-dimethylaminophenyl)carbanate (33.6 g, 0.13 mol), chlorotrimethylsilane (14.3 g, 0.13 mol) and triethylamine in 600 ml dry toluene was refluxed for three hours. The reaction mixture was allowed to cool to room temperature. The precipitated triethylamine hydrochloride was filtered and washed with toluene. The residual oil after solvent removal was distilled under reduced pressure to yield 17.2 grams of the p-N,N-dimethylaminophenyl isocyanate (59-62°C/0.2 mm) (lit.⁶³ 60°/0.25 mm).

1-Ethoxycarbonyl-1,4-(p-N,N-dimethylaminophenyl)-semi-carbazide 98.

p-N,N-dimethylaminophenyl isocyanate (12.0 g, 0.074 mol) in

benzene was added dropwise to a benzene solution of 7.5 grams (0.0721 mol) ethyl carbazate in a 500 ml flask cooled via ice bath and equipped with a mechanical stirrer, reflux condenser, thermometer and addition funnel. The rate of addition was such that the temperature remained at 10-15°C. After addition, the solution was allowed to warm to room temperature and stirring continued for 15 minutes. A fine white precipitate formed in high yield during the original addition which when filtered and dried melted at 165-8°C. NMR signals were found at (DMSO-d₆) 1.35δ (T, 3), 2.9δ (s, 6), 4.1δ (Q, w), 7.9δ (Q, 4), 7.9δ (s, 1), 8.3δ (s, 1) and 8.7δ (s, 1).

4-(p-N,N-Dimethylaminephenyl) urazole 97.

1-Ethoxycarbonyl-4-(p-N,N-dimethylaminophenyl)semi-carbazide (6 g, 0.023 mole) was added to 200 ml 4M KOH and heated to 75°C for 15 minutes. The solution was filtered to remove any insoluble material and cooled in an ice bath to approximately 20°C. Concentrated HCl was used to neutralize the basic solution making sure to keep temperature below 25°C by controlled addition. At the neutral point, the solution became pale red and crystallization began. Great care was taken as over acidification resulted in dissolution of the solid urazole via protonation of the tertiary amine. A pale, off-white powder was obtained in excellent yield which melted at 268-7°C. Infrared absorbances were found at (Nujol) 3200 (w), 2900 (s), 1770 (w), 1680 (s, broad), 1615 (m), 1525 (m), 1460 (s), 1380 (s), 1370 (m), 1230 (w),

1195 (w), 1170 (w), 1130 (w), 1100 (w), 1065 (w), 950 (w), 815 (w), 795 (w), 765 (w), 720 (w), and 665 (w) cm^{-1} .

NMR signals were found at ($\text{DMSO}-d_6$) 2.9 δ (s, 6), 6.9 δ (Q, 4), 10.2 δ (s, 2). Mass spectral molecular ion at 206 m/e.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$: C, 50.00; H, 5.85; N, 23.64. Found: C, 50.42; H, 5.88; N, 23.52. Twenty-four hours of heating at 140°C/0.05 mm Hg. was ineffective at removing the H_2O .

1,2-Dihydro-4-(p-phenyldimethylammonium chloride)-1,2,4-triazoline-3,5-dione 99.

p-N,N-dimethylaminophenyl urazole, (97), (3 g, 1.3×10^{-2} mol) was dissolved in 150 ml dry THF. Concentrated HCl was then added dropwise followed by immediate precipitation of a white solid. This was filtered and washed twice with THF and ethyl ether, m.p. 250°C. Infrared absorbances were found at (Nujol) 3100 (m), 2900 (s), 2650 (m), 2600 (w), 2450 (w), 1770 (w), 1710 (s), 1600 (w), 1520 (m), 1500 (w), 1490 (w), 1460 (s), 1420 (m), 1380 (m), 1360 (m), 1210 (w), 1190 (w), 1135 (w), 1125 (w), 1085 (w), 1065 (w), 1025 (w), 990 (w), 900 (w), 855 (w), 800 (m), 765 (w), 740 (m), 680 (w), 650 (w), and 630 (w) cm^{-1} . NMR signals were found at (D_2O) 7.7 δ (Q, 4), 3.3 δ (s, 6).

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$: C, 43.79; H, 5.43; N, 20.43. Found: C, 43.79; H, 5.64; N, 20.18.

1,2-Dihydro-4-(p-phenyltrimethylammonium iodide) 1,2,4-triazoline-3,5-dione 100.

p-N,N-dimethylaminophenyl urazole (97), (1.1 g, 0.005 mol) was placed in 100 ml THF along with 0.9 g (6.3×10^{-3} mol)

methyl iodide and stirred overnight at room temperature. A pale solid was obtained, m.p. $230-32^{\circ}\text{C}$. Infrared absorbances were found at (Nujol) 3100 (s), 2900 (s), 2710 (w), 1780 (m), 1705 (s), 1525 (m), 1460 (s), 1380 (m), 1310 (w), 1295 (w), 1225 (w), 1120 (w), 1200 (w), 960 (w), 940 (w), 855 (w), 790 (w), 770 (w), 735 (w), 655 (w), and 635 (w) cm^{-1} . NMR signals were found at (D_2O) 7.8 δ (Q, 4), 3.6 δ (s, 9).

Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_2\text{I}\cdot 2\text{H}_2\text{O}$: C, 33.16; h, 4.66; N, 14.07. Found: C, 33.40; H, 4.47; N, 13.87.

C. Oxidation of the 4-Substituted Urazoles

Oxidation procedure for urazoles was essentially the same and is give here. Each urazole is discussed below to mention discrepencies.

General procedure

Anhydrous sodium sulfate, 25.0 g, was placed into a 500 ml Erlenmeyer flask with 200 ml of methylene chloride and 6.0 g. of 4-substituted urazole. The slurry was stirred by a magnetic stirrer and cooled to $0-5^{\circ}\text{C}$ with an ice water bath. Fifteen drops fuming nitric acid was added to the slurry. After a few minutes a deep red color developed. After approximately 15-20 minutes, the solution was filtered. More CH_2Cl_2 was added to the solid and six drops fuming nitric added to this and the process repeated. The filtered methylene chloride solutions were combined and washed with two 100 ml portions of distilled water in a 500 ml separatory funnel. The methylene chloride solution was then dried over MgSO_4 for 24 hours. The red solid, after solvent evaporation,

was then sublimed in most cases. All of the oxidized products were found to have the greatest shelf life when stored in a dried container under N_2 in the freezer.

4-Phenyl-1,2,4-triazoline-3,5-dione

Purification of this was accomplished by sublimation at $70-75^{\circ}$ under a vacuum of less than 0.5 mm Hg. (high yield).

4-Methyl-1,2,4-triazoline-3,5-dione

The light red fluorescent appearing powder was purified by sublimation at less than 0.1 mm and a temperature between 50 and 60° (high yield).

4-(p-Tolyl)-1,2,4-triazoline-3,5-dione

The brilliant red crystals were purified via vacuum sublimation at $80^{\circ}C$ and less than 0.3 mm Hg. (high yield).

4-(m-Tolyl)-1,2,4-triazoline-3,5-dione

The brilliant red crystals were purified via vacuum sublimation at $80^{\circ}C$ and less than 0.1 mm Hg. (high yield).

4-(p-Methoxyphenyl)-1,2,4-triazoline-3,5-dione

The deep purple-red crystals were purified via vacuum sublimation at $85^{\circ}C$ and less than 0.03 mm Hg. in low yield over a 60 hour period.

4-(p-Nitrophenyl)-1,2,4-triazoline-3,5-dione

The pale red crystals were purified by precipitation from dry hexane in a minimum ethyl acetate solution. Sublimation was not attempted due to the potentially explosive character of this compound.

4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione

The light pink solid was dissolved in minimal ethyl

acetate and precipitated from dry hexane twice. This material was used without further purification.

4-(p-carbethoxyphenyl)-1,2,4-triazoline-3,5-dione

The red solid was reprecipitated from hexane.

4-(p-carboxypehnyl)-1,2,4-triazoline-3,5-dione

The pale red solid was reprecipitated from hexane.

4-(p-N,N-Dimethylaminophenyl)-1,2,4-triazoline-3,5-dione

Oxidation Procedure

To 0.103 grams (0.0005 mol) p-N,N-dimethylaminophenyl urazole dissolved in 95 ml dry DMSO in a 100 ml, 0.10 g (0.00050 mol) of p-toluene sulfonyl isocyanate was added. Volume was brought up to 100 ml and the reaction allowed to proceed at room temperature for 15 minutes. The solution turned purple rapidly with a slight evolution of gas, assumed to be CO₂ as per the proposed mechanism for this oxidation method.¹⁹ This compound was not isolated in the crystalline form, nor was it employed in any of this work.

D. 1:1 and 2:1 Adducts of 4-Substituted-1,2,4-triazoline-3,5-dione and β-Dicarbonyls

3-(2-Hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-2,4-pentane diene 26

PhTD (0.868 g, 0.0049 mol) dissolved in 25 ml reagent grade methylene chloride was added to 1.5 g (0.0147 mol) 2,4-pentanedione in 25 ml of the dried methylene chloride. The color was depelted in about 15 minutes. Solvent was then evaporated off and the resulting oil crystallized overnight. Crystals were purified by recrystalization in an ethanol

water mixture yielding 1.2 g (87%) white powder melting at 171-173°C. Infrared absorbances were found at (KBr) 3050 (b), 2800 (m), 1770 (s), 1700 (b), 1600 (b), 1460 (s), 1410 (s), 1360 (s), 1250 (s), 1210 (s), 1150 (s), 1090 (s), 1000 (b), 910 (s), 820 (s), 750 (s), 720 (s), 690 (s), and 630 (s) cm^{-1} . Nuclear magnetic resonance signals were found at (acetone- d_6) 2.15 δ (s), 7.5 δ (s), 8.3 δ (s, broad) and 15.9 δ (s, broad). Molecular ion : 275 m/e.

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}_3$: C, 56.72; H, 4.73; N, 15.23.
Found: C, 56.42; H, 4.97; N, 14.90.

3-(Bis-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-2,4-pentanedione 24

PhTD (0.86 g, .0049 mol) in 50 ml methylene chloride was added directly to .245 g (0.00245 mol) 2,4-pentanedione in 50 ml of the same solvent. The reaction was complete in approximately 20 hours. Recrystallization yielded the 1:1 adduct, 26, as major product. The reaction was repeated in acetonitrile. Recrystallization of the crude solid from chloroform gave 0.5 g of white solid, 24, m.p. 215 (dec). Infrared absorbances were found at (KBr) 3150 (b), 1800 (s), 1720 (b), 1600 (s, m), 1510 (s), 1430 (s), 1380 (s), 1250 (b), 1180 (w), 1150 (s), 1080 (w), 1030 (s), 810 (s), 780 (s), 725 (w), 700 (s), and 625 (b) cm^{-1} . NMR signals were found at (DMSO- d_6) 2.40 δ (s), 7.45 δ (m), 10.6 δ (s, broad). No mass spectral molecular ion was observed.

Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_6\text{O}_6$: C, 56.00; H, 4.00; N, 18.67.
Found: C, 56.08; H, 4.11; N, 18.74.

3-[2-Hydro-4-(p-tolyl)-1,2,4-triazoline-3,5-dionyl]-2,4-pentanedione, 35.

4-(p-tolyl)-1,2,4-triazoline-3,5-dione (0.92 g, 0.0049 mol) in 25 ml reagent grade methylene chloride was added to 1.5 g (0.014 mol) 2,4-pentanedione in 25 ml of the dried methylene chloride. The reaction was complete as noted by decoloration in approximately 15 minutes. The solvent was rotoevaporated off at which time crystals having a crude melting point formed. These were recrystallized in an EtOH-H₂O mixture to give 1.0 grams (70%) of a white powder. Infrared absorbances were found at (KBr) 3100 (b), 2900 (sh), 1770 (s), 1700 (b), 1600 (b), 1460 (s), 1410 (s), 1360 (s), 1250 (s), 1210 (s), 1150 (s), 1090 (s), 1000 (b), 910 (s), 820 (s), 750 (s), 720 (s), 690 (s), and 630 (s) cm⁻¹. NMR signals were found at (CDCl₃) 2.15δ (s), 2.4δ (s), 7.3δ (s), 15.3δ (s, broad). Molecular ion: 289 m/e.

Anal. Calcd. for C₁₄H₁₅N₃O₄: C, 58.13; H, 5.19; N, 14.53. Found: C, 57.76; H, 5.24; N, 14.30.

Ethyl-2-(2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-3-one-butrate, 32

PhTD (1.0 g, 0.005 mol) in 25 ml reagent grade CH₂Cl₂ was added to 4.45 g (0.0342 mol) ethylacetoacetate. The reaction was complete in approximately 15 minutes. During rotoevaporation, crystals fell out of the warm solution. These were dried and gave a melting point of 150-5°C. Further drying in pistol at 0.03 mm Hg. and 136°C resulted in decomposition of the solid. A second set of crystals (0.42 g,

24%) fell from the original solution. These were dried at 35° in a vacuum oven and gave a melting point of $152-4^{\circ}$ (32). Infrared absorbances were found at (KBr) 3100 (b), 2850 (sh), 1780 (s), 1700 (s), 1660 (s), 1610 (s), 1500 (s), 1400 (s), 1320 (s), 1260 (w), 1220 (s), 1185 (s), 1140 (w), 1085 (w), 1060 (s), 1000 (w), 800 (b), 770 (w), 700 (b) and 630 (w) cm^{-1} . NMR signals were found at (Acetone- d_6) 1.25 δ (T), 1.3 δ (T), 2.1 δ (s), 2.45 δ (s), 4.25 δ (Q), 4.30 δ (Q), 5.6 δ (s), 7.45 δ (s), 12.3 δ (s, broad, existed as 75% enolized tautomer in this solvent). Molecular ion: 302 m/e.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_5$: C, 55.08; H, 4.92; N, 13.77. Found: C, 55.06; H, 4.94; N, 13.82.

Ethyl-1,2-(bis-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-3-one-butyrate, 33.

PhTD (0.6 g, 0.0034 mol) in 20 ml reagent grade methylene chloride was added to 0.4 g (0.0034 mol) ethylacetoacetate in 20 ml of the dry methylene chloride. The reaction was complete in 24 hours as noted by decoloration. The CH_2Cl_2 was rotoevaporated away and the resulting oil dissolved in ethanol. Water was added to the warm solution until cloudiness persisted. This mixture was heated until solution was obtained. On slow cooling crystals formed having a melting point of $199-202^{\circ}\text{C}$. Infrared absorbances were found at (KBr) 3520 (s), 3120 (b), 2960 (w), 2900 (w), 2820 (w), 1800 (s), 1740 (b), 1520 (s), 1430 (b), 1370 (s), 1290 (s), 1260 (s), 1230 (s), 1190 (s), 1160 (s), 1080 (s), 1015 (s), 870 (w), 810 (m), 770 (m), 715 (s), 700 (w), 680 (s), and 640 (w) cm^{-1} .

NMR signals were found at: 1.35 δ (T), 2.47 δ (s), 4.47 δ (Q), 7.4 δ (s). No molecular ion was observed in the mass spectrum.

Anal. Calcd. for $C_{22}H_{20}N_6O_7$: C, 55.00; H, 4.17; N, 17.45. Found: C, 54.65; H, 4.34; N, 17.12.

Ethyl-2-[bis-2-hydro-4-(p-tolyl)-1,2,4-triazoline-3,5-dionyl]-3-one-butyrate, 34.

4-(p-tolyl)-1,2,4-triazoline-3,5-dione (0.2 g, 0.0015 mol) in 20 ml reagent grade methylene chloride was added to 0.14 g (0.0015 mol) ethyl acetoacetate in 20 ml of dry solvent. The reaction was complete in 24 hours. Some needle crystals of melting point 228-31 $^{\circ}$ formed from this solution. On roto-evaporation of solvent, an oil was obtained which was crystallized by dissolving in ethanol and using water as the non-solvent. Needle crystals were obtained overnight, m.p. 228-31. Infrared absorbances were found at (KBr) 3540 (s), 3320 (b), 3120 (b), 2950 (w), 2820 (w), 1800 (s), 1730 (s), 1520 (s), 1430 (b), 1370 (s), 1290 (s), 1265 (s), 1230 (s), 1190 (s), 1160 (s), 1080 (s), 1020 (s), 870 (m), 810 (m), 770 (b), 717 (s), 680 (s), and 650 (s) cm^{-1} . NMR signals were found at 1.3 δ (T), 2.35 δ (2 singlets), 4.35 δ (Q), 7.2 δ (s), 10.3 δ (s, broad). Mass spectral parent ion was not obtainable.

Anal. Calcd. for $C_{24}H_{24}N_6O_7$: C, 56.69; H, 4.72; N, 16.54. Found: C, 56.75; H, 4.78; N, 16.57.

2-(2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-1,3-cyclohexanedione, 29.

PhTD (0.44 g, 0.0025 mol) in reagent grade methylene chloride was added dropwise to a rapidly stirred solution of

3.0 g (0.025 mol) recrystallized 1,3-cyclohexanedione in CH_2Cl_2 . Reaction was instantaneous noted by immediate decoloration of the triazolinedione color. The solvent was rotoevaporated and the resulting solid redissolved in 50 ml CHCl_3 . Crystals formed over a 48 hour period, m.p. 211 (dec). Infrared absorbances were found at (KBr) 3120 (broad), 1770 (s), 1700 (b), 1640 (b), 1560 (b), 1490 (s), 1450 (w), 1410 (b), 1360 (s), 1350 (w), 1320 (s), 1280 (s), 1240 (b), 1180 (s), 1130 (s), 1060 (w), 980 (s), 905 (w), 880 (m), 760 (s), 740 (w), 720 (w), and 690 (s) cm^{-1} . NMR signals were found at ($\text{DMSO}-d_6$) 1.9 δ (m), 2.45 δ (m), 7.4 δ (s), 12.77 δ (s). Molecular ion: 2.87 m/e.

Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4$: C, 58.54; H, 4.53; N, 14.63. Found: C, 58.57; H, 4.54; N, 14.57.

2-(Bis-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-1,3-cyclohexanedione, 30.

PhTD (1.0 g, 0.005 mol) in 25 ml reagent grade methylene chloride was added to a 0.35 g (0.0029 mol) 1,3-cyclohexanedione in 25 ml CH_2Cl_2 in a 200 ml Erlenmeyer flask. The reaction was complete in four hours. After removal of 50 ml of the solvent, crystals fell from solution. These were recrystallized from a CH_2Cl_2 -Acetone cosolvent mixture to give a white powder having a melting point of 179-82°C. Infrared absorbances were found at (KBr) 3370 (s), 3250 (s), 3100 (b), 2940 (s), 1770 (s), 1600 (b), 1580 (w), 1485 (s), 1400 (b), 1200 (b), 1130 (s), 1010 (w), 885 (w), 740 (b), and 670 (b) cm^{-1} . NMR signals were found at (Acetone- d_6) 2.3 δ (m),

3.0 δ (T), 6.4 δ (s) (exchanges with D₂O), 7.5 δ (s). Mass spectral molecular ion was unobtainable.

Analysis: Two analysis gave low carbon nitrogen and high hydrogen based on C₂₂H₁₈N₆O₆ implying hydration. Assuming 1:1 adduct: H₂O: Calculated for C₂₂H₁₈N₆O₆·H₂O: C, 55.0; H, 4.16; N, 17.50. Found: C, 54.89; H, 4.19; N, 17.40.

2-(Bis-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-5,5-dimethyl-1,3-cyclohexanedione, 41.

5,5-Dimethyl-1,3-cyclohexanedione (0.20 g, 1.43x10⁻³ mol) in 50 ml ethyl acetate was added to 0.5 g (2.86x10⁻³ mol) PhTD (1) in 50 ml of this solvent. The reaction was complete in one hour. Crystallization was accomplished by addition of hexane to cloudiness, heating to again obtain solution and subsequent slow cooling. A white powder having a melting point of 218 (dec) was obtained. Infrared absorbances were found at (Nujol) 3200 (m), 3100 (m), 2900 (s), 1792 (w), 1770 (m), 1740 (s), 1700 (s), 1600 (w), 1505 (m), 1495 (w), 1460 (s), 1415 (m), 1380 (m), 1320 (w), 1270 (m), 1240 (w), 1220 (w), 1185 (m), 1160 (m), 1080 (w), 1065 (w), 1030 (w), 1010 (w), 970 (w), 940 (w), 920 (w), 845 (w), 805 (w), 770 (m), 760 (w), 740 (w), 715 (w), 705 (w), 690 (w), and 645 (m) cm⁻¹. NMR signals were found at (DMSO-d₆) 7.5 δ (s, 5), 3.0 δ (s, 4), 1.1 δ (s, 6).

Anal. Calcd. for C₂₄H₂₂N₆O₆: C, 58.78; H, 4.49; N, 17.14. Found: C, 59.02; H, 4.55; N, 17.49.

2-(2-Hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-1,3-phenyl-1,3-propanedione, 37.

PhTD (0.5 g, 0.00285 mol) in 40 ml reagent grade THF was added dropwise to 40 ml of rapidly stirred solution containing 3.1 g (0.0143 mol) dibenzoyl methane. The reaction was instantaneous as shown by decoloration to a pale yellow solution. The crude solid obtained from rotoevaporation of the solvent was recrystallized from a THF-hexane mixture and the resulting crystals washed with cold acetone. Needle crystals (1.1 g, 97%) having a melting point of 189-91°C were obtained.

Infrared absorbances were found at: 3500 (w), 3260 (b), 3080 (s), 2960 (s), 1790 (s), 1800 (b), 1600 (s), 1580 (s), 1500 (s), 1430 (m), 1280 (m), 1240 (m), 1200 (w), 1180 (w), 1140 (w), 1000 (s), 985 (w), 930 (w), 820 (m), 760 (m), and 690 (m) cm^{-1} . NMR signals were found at (Acetone- d_6) 7.31 (s), 7.42 (s), 7.55 (m), 8.1 (m). Molecular ion was found at 399 m/e.

Anal. Calcd. for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_4$: C, 69.18; H, 4.26; N, 10.53. Found: C, 69.40; H, 4.36; N, 10.64.

2-(Bis-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-pentandione, 38.

PhTD (0.5 g, 0.00285 mol) in 25 ml THF was added to 0.32 g (0.00142 mol) dibenzoyl methane. The reaction was complete in 24 hours. Rotoevaporated solid was recrystallized from CHCl_3 -hexane giving a fine white powder melting at 160-2°C. Infrared absorbances were found at (Nujol) 3200 (w), 2950 (s), 2860 (s), 1800 (s), 1740 (s), 1680 (s), 1600 (s), 1580 (w), 1500 (m), 1460 (s), 1420 (w), 1380 (w), 1260 (w), 1220 (w), 1150 (w),

1020 (w), 890 (2), 820 (w), 760 (w), 720 (w), 700 (w), 690 (w), and 640 (w) cm^{-1} . NMR signals were found at (Acetone- d_6) 7.4 δ (m), 7.45 δ (s), 8.1 δ (m). No mass spectral molecular ion was found.

Anal. Calcd. for $\text{C}_{31}\text{H}_{22}\text{N}_6\text{O}_6$: C, 64.81; H, 8.83; N, 14.63. Found: C, 64.72; H, 4.13; N, 14.42.

2-(Bis-hydro-4-methyl-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione, 39.

4-Methyl-1,2,4-triazoline-3,5-dione (0.25 g, 0.0023 mol) in 30 ml acetone was added dropwise to 1.25 g (0.005 mol) dibenzolyl methane in 45 ml of the solvent in a 100 ml Erlenmeyer flask. Reaction was complete in 15 minutes. Solution was rotoevaporated away and the resulting yellow oil was crystallized from THF-hexane mixture to give needle crystals of m.p. 164-6 $^{\circ}\text{C}$. Infrared absorbances were found at (Nujol) 3200 (m), 2900 (s), 1770 (w), 1720 (w), 1680 (s), 1610 (w), 1600 (w), 1580 (w), 1460 (s), 1380 (w), 1345 (w), 1295 (w), 1265 (w), 1180 (w), 1080 (w), 1040 (w), 1005 (w), 985 (w), 940 (w), 910 (w), 840 (w), 830 (w), 795 (w), 765 (w), 740 (w), 690 (w), 660 (w) and 625 (w) cm^{-1} . NMR signals were found at (DMSO- d_6) 3.1 δ (s), 7.18 δ (s, exchanged with D_2O), 7.6 δ (m), 8.1 δ (m).

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_4$: C, 64.0; H, 4.45; N, 12.46. Found: C, 63.65; H, 4.90; N, 13.01.

2-(2-Hydro-4-methyl-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione, 40

MeTD (0.25 g, 0.0023 mol) in 35 ml reagent grade

acetone was mixed with 0.25 g (0.00115 mol) dibenzoyl methane in 35 ml of the acetone. After 48 hours, red color was gone. The solvent was rotoevaporated off and the resulting crystals recrystallized from a THF (min)-hexane mixture. A gel-like precipitate resulted. This was filtered, yielding a white powdery solid which upon drying in vacuum oven gave a melting point of $164-6^{\circ}\text{C}$. The solid was found to be hydrated. Attempts to remove this resulted in decomposition of the adduct. Infrared absorbances were found at 3200 (w), 2900 (s), 1800 (m), 1720 (s), 1600 (w), 1580 (w), 1460 (m), 1400 (m), 1380 (w), 1290 (w), 1260 (w), 1220 (w), 1180 (w), 1000 (w), 940 (m), 920 (w), 900 (w), 820 (w), 800 (m), 760 (w), 730 (w), 690 (w), 640 (w), and 610 (w) cm^{-1} . NMR signals were found at ($\text{DMSO}-d_6$) 2.15 δ (s), 6.8 δ (m), 7.2 δ (m).

Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_6\text{O}_6$: C, 51.85; H, 4.52; N, 17.20. Found: C, 51.99; H, 4.51; N, 16.88.

E. Copolymers of 4,4'-(4,4'-Diphenylmethylene)-bis-1,2,4-Triazoline-3,5-dione (16) and β -Dicarbonyls.

Copolymerization of 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione (16) and 2,4-Pentanedione, 44.

4,4'-(4,4'-Diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione (0.54 g, 0.0015 mol) in 30 ml ethylacetate was added to 0.15 g (0.0015 mol) pentanedione in 30 ml dry ethylacetate. After 12 hours decolorization was complete and a solid came out of solution. This was dissolved in a minimum amount of THF and precipitated from a 50:50 mixture of acetone-diethyl ether. This process was repeated and the resulting solid

dried in a vacuum oven overnight at 60°C/1mm Hg. (T_{dec} 229°C) Infrared absorbances were found at (Nujol) 3450 (w), 3200 (w), 2900 (s), 1775 (w), 1700 (s), 1620 (w), 1515 (w), 1460 (s), 1420 (w), 1380 (w), 1280 (w), 1230 (w), 1140 (w), 1020 (w), 920 (w), 760 (w), and 720 (w) cm^{-1} . NMR signals were found at (DMSO- d_6) 7.3 δ (s, broad), 3.5 δ (s, broad), 2.3 δ (s, broad) 2.15 δ (s, broad).

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}$: C, 57.4; H, 3.90. Found: C, 56.95; H, 4.11.

Copolymers of 16 and ethylacetoacetate, 45; 16 and dibenzoylmethane, 46; 16 and 1,3-cyclohexanedione, 47.

The copolymers, 45, 46, and 47 were prepared and isolated in the manner described for 16 and 2,4-pentanedione above. Spectral and analysis data are given below.

45, NMR signals were found at (DMSO- d_6) 7.4 δ (s, broad) 4.2 δ (m, broad), 2.3 δ (s, broad), 1.2 δ (t, broad).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{N}_6\text{O}_6$: C, 56.1; H, 4.07. Found: C, 55.84; H, 4.24.

46, Infrared absorbances were found at (Nujol) 3200 (m), 2900 (s), 1780 (w), 1710 (s), 1600 (w), 1515 (w), 1460 (s), 1380 (w), 1260 (w), 1220 (w), 1180 (w), 1155 (w), 1015 (w), 990 (w), 820 (w), 765 (w), 720 (w), 690 (w), and 640 (w) cm^{-1} . NMR signals were found at (DMSO- d_6) 4.05 δ (s, broad), 7.4 δ (s, broad), 7.5 δ (s, broad), 8.0 δ (s, broad).

47, Infrared absorbances were found at (Nujol) 3450 (w), 3200 (w), 2900 (s), 1765 (w), 1700 (s), 1600 (w), 1515 (w), 1460 (s), 1375 (w), 1405 (w), 1230 (w), 1180 (w), 1140 (w),

1020 (w), 995 (w), 820 (w), 765 (w), and 720 (w) cm^{-1} .

NMR signals were found at (DMSO- d_6) 10 δ (d, broad, 7.6 δ (s, broad), 7.9 δ (s, broad), 3.7 δ (s, broad), 2.4 δ (m, broad).

F. Polymer Modification and Model Compound Synthesis

General Procedure for addition of 4-phenyl-1,2,4-triazoline-3,5-dione, 1; 4-methyl-1,2,4-triazoline-3,5-dione and 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione, 16; to dienic polymers, 54, 55, 56 and 57.

Samples of the commercial unsaturated polymers (number of moles based on repeating unit weight) were dissolved in approximately 400 ml dry benzene and filtered to assure complete solubilization. Solution of the triazolinedione in benzene was added dropwise to the rapidly stirred polymer solution. Additions of less than 10% triazolinedione: repeating unit were soluble in this solvent, while the larger ones were not and polymer began to precipitate many times before the addition was complete. These precipitated polymers appeared to be swollen by the solvent and in most cases the reaction gave complete decolorization of the triazolinedione implying complete reaction. Analysis of the modified polymers was limited to percent nitrogen. Infrared absorbances were found for PhTD modified polymers at (CS_2) 3400 (s), 3200 (s), 2900 (m), 2300 (m), 2160 (s), 1770 (s), 1700 (s), 1580 (m), 1520 (s), 1280 (m), 1240 (m), 1130 (m), 1070 (w), 1020 (w), 970 (m), 910 (m), 870 (w), 770 (s), and 700 (m) cm^{-1} . Infrared absorbances were found for MeTD modified polymers at (Nujol) 3450 (w), 3200 (w), 1760 (m), 1700 (s), 1460 (s),

1380 (m), 1300 (w), 1240 (w), 1155 (w), 1010 (w), 975 (w), 760 (w), and 720 (w) cm^{-1} . Viscometry of the modified polymers was carried out in 0.8M KOH solution.

4-Phenyl-1,2,4-triazoline-3,5-dione addition to the maleic anhydride-furan copolymer, 38.

Maleic anhydride-furan copolymer, 38, (0.075 g , $4.52 \times 10^{-4} \text{ mol}$) in 20 ml acetone was combined with a 20 ml solution of PhTD (1). After 40 hours, the reaction was complete as determined by decoloration of the solution. The polymer was precipitated from hexane to give a light brown solid ($T_g = 158^\circ$). Infrared absorbances were found at (Nujol) 3200 (m), 2900 (s), 2600 (m), 1850 (m), 1780 (s), 1700 (s), 1600 (w), 1500 (w), 1460 (s), 1380 (m), 1240 (m), 1180 (m), 1080 (m), 940 (m), 820 (w), 770 (w), 730 (w) and 700 (w) cm^{-1} . NMR signals were found at (Acetone- d_6) 7.5δ (s), 6.15δ (s), 5.4δ (s), 4.5δ (s), 3.4δ (d), 1.6δ (s) all very broad.

1-(2-Butene)-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dione, 51.

1-Butene was passed into a 3-necked 100 ml flask equipped with a dry ice condenser. After approximately 15 ml was collected, 30 ml dry reagent grade methylene chloride were added to aid in dissolution of PhTD. PhTD (0.7 g , 0.004 mol) were added and allowed to react at the temperature of the solvent mixture. The temperature was allowed to raise to room temperature by removing the condenser. After the excess butene had evaporated, CH_2CL_2 was removed by rotoevaporation leaving a white solid having a 10° melting point range. This solid was recrystallized in an ethanol water mixture. Fine

white needle crystals formed after three days (m.p. 126.5-127.5°) in 70% yield. Infrared absorbances were found at (CHCl_3) 3000 (b), 1770 (s), 1700 (s), 1600 (w), 1500 (s), 1430 (s), 1360 (w), 1285 (w), 1240 (w), 1140 (s), 1030 (w), 970 (s), 925 (w), and 695 (b) cm^{-1} . NMR signals were found at ($\text{DMSO}-d_6$) 1.7 δ (d, 3), 4.1 δ (d, 2), 5.6 δ (m, 2), 7.4 δ (s, 5).

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2$: C, 62.34; H, 5.63; N, 18.18. Found: C, 62.48; H, 5.59; N, 18.11.

1-(4-Methyl-2-pentene)-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dione, 52.

PhTD (1) (1.0 g, 0.0057 mol) in 25 ml chloroform was added dropwise to a rapidly stirred solution of 4-methyl-1-pentene (4.7 g, 0.057 mol) in 25 ml chloroform. Decolorization was immediate with the first additions and became slower as more PhTD was added, taking 15 minutes after the last addition. The solvent was rotoevaporated off and the resulting oil recrystallized in an ethanol-water mixture to give after two days very fine needles, m.p. 108-110°C. Infrared absorbances were found at (Nujol) 3180 (w), 3020 (w), 2900 (s), 1770 (m), 1700 (s), 1600 (w), 1505 (m), 1460 (s), 1380 (m), 1370 (m), 1280 (w), 1255 (w), 1220 (w), 1175 (w), 1150 (w), 1140 (w), 1075 (w), 1030 (w), 975 (m), 915 (w), 850 (w), 820 (w), 775 (m), 710 (m), and 650 (m) cm^{-1} . NMR signals were found at ($\text{Acetone}-d_6$) 0.9 δ (d, 6), 2.2 δ (m, 1), 4.1 δ (d, 2), 5.6 δ (m, 5). Molecular ion at 259 m/e.

Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 62.68; H, 7.08; N, 15.67. Found: C, 62.98; H, 6.91; N, 15.81. Attempted

removal of water of hydration by high vacuum and heat resulted in decomposition.

1-(4-Methyl-2-pentene)-2-hydro-4-(p-nitrophenyl-1,2,4-triazoline-3,5-dione, 53

p-NitroPhTD (1.0 g, 0.0045 mol) in 25 ml CHCl_3 was added dropwise to a rapidly stirred 25 ml chloroform solution of 3.8 g (0.045 mol) 4-methyl-1-pentene. Reaction was complete in 15 minutes. Solvent was rotoevaporated away and the resulting solid recrystallized from ethanol-water mixture to give yellow needle crystals in low yield, m.p. $158-160^\circ$. Infrared absorbances were found at (Nujol) 3150 (w), 2900 (s), 1770 (w), 1700 (s), 1600 (w), 1515 (w), 1500 (w), 1460 (s), 1380 (m), 1340 (m), 1215 (w), 1130 (w), 1110 (w), 980 (w), 915 (w), 855 (m), 760 (w), and 720 (w) cm^{-1} . NMR signals were found at (Acetone) 0.95 δ (d, b), 2.3 δ (m, 3), 4.2 δ (d, 2), 5.7 δ (m, 2), 8.15 δ (Q, 4). Molecular ion at 304 m/e.

1-(2-Butene)-2-hydro-4-methyl-1,2,4-triazoline-3,5-dione, 50.

MeTD (4.0 g) were added to a three-necked 100 ml flask equipped with dry ice condenser in which approximately 15 ml 1-butene was collected. Reagent grade methylene chloride (30 ml) were added to aid in dissolution. The reaction was complete as evidenced by color loss of the red solution in 15 minutes. The reflux condenser was removed and 1-butene allowed to evaporate. The remaining solvent was then rotoevaporated away leaving a pale oil which was recrystallized from MeCl_2 in low yield to give colorless crystals, m.p. $45-46^\circ\text{C}$.

Infrared absorbances were found at (Nujol) 3100 (s), 2900 (s), 1760 (s), 1700 (s), 1460 (s), 1410 (w), 1380 (w), 1360 (w), 1305 (w), 1275 (w), 1240 (m), 1220 (w), 1165 (w), 1115 (w), 1065 (w), 1030 (m), 975 (m), 955 (m), 900 (w), 780 (s), 725 (w), 695 (w) and 630 (m) cm^{-1} . NMR signals were found at (Acetone- d_6) 1.5 δ (d, 3), 2.0 δ (s, 3), 4.1 δ (d, 2), 5.6 δ (m, 2), 6.6 δ (broad s, 1).

Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2$: C, 49.70; H, 6.50; N, 24.85.
Found: C, 49.54; H, 6.71; N, 24.80.

G. General Synthesis

Preparation of chloromethyl isocyanate

To a flamed 500 ml flask equipped with reflux condenser, thermometer, mechanical stirrer and addition funnel was added 33 g (0.5 mol) NaN_3 in 150 ml deionized water. To this solution cooled to 10-15°C, 44 g (0.44 mol) chloroacetylchloride in benzene was added dropwise maintaining this temperature. The organic solution turned dark red rapidly and the reaction was allowed to go for eight hours. The cooled benzene layer was separated and dried overnight over MgSO_4 . This azide solution was rearranged to the isocyanate by dropwise addition to benzene heated to 75°C in a 500 ml flask equipped with condenser and thermometer. The addition took approximately three hours as the rate of addition was controlling gas evolution during the rearrangement. The volatile isocyanate distilled over with benzene at 80°C. IR showed the characteristic strong isocyanate absorption at 2300 cm^{-1} along with peaks characteristic of benzene.

The reaction was repeated in toluene in an attempt to have a solvent from which the product can be separated via distillation. Distillation of the isocyanate resulted in stabilization at 105°. The distillate gave the characteristic 2300 cm⁻¹ infrared band. NMR shows the substituted methyl absorbance at 4.3δ along with absorptions for toluene.

The reaction was repeated in xylene and the product was obtained at 120mm Hg/50°C. Again NMR and IR show both the isocyanate and xylene.

The reaction was attempted in synthetic octane. After this mixture stirred at 15-20° for eight hours, three layers were noted. These were separated and each placed over MgSO₄. Two hours later, a violent explosion occurred. This synthesis was no longer attempted.

Infrared absorbances of the compound distilled from toluene (drop of distillate on NaCl plates) were found at 3100 (s), 3080 (s), 3040 (s), 3000 (s), 2940 (s), 2890 (s), 2280 (intense), 1950 (w), 1860 (w), 1780 (w), 1610 (w), 1500 (s), 1460 (m), 1380 (s), 1305 (s), 1220 (w), 1180 (m), 1080 (s), 1030 (s), 890 (s), 725 (s), and 590 (s) cm⁻¹.

Attempted chloromethylation of 4-phenyl urazole, 2

In an oven dried micro RB flask equipped with condenser and CaCl₂ drying tube, 1.0 g (0.005 mol) ϕ -urazole was added to 4 g (0.015 mol) of chloromethyl methyl ether, 0.1 g anhydrous ZnCl₂ and 5 ml anhydrous ethyl ether. This was refluxed for two hours after which time a tan precipitate fell from solution. The solvent was allowed to evaporate

away and the crude solid extracted with water to separate the organic products from the ZnCl_2 . NMR of the crude product shows absorption in the chloromethyl region of 5.1 δ as well as broadened signals. Work was discontinued due to the toxic nature of the ether reagent.

p-Bromomethyl-phenyl isocyanate

1,3-Dibromo-5,5-dimethyl hydantoin, 90, (5.0 g, 0.018 mol), phenylisocyanate (10.0 g, 0.0075 mol) and dibenzoyl peroxide (0.16 g, 0.0068 mol) were mixed with carbon tetrachloride in a flamed dried 500 ml flask equipped with reflux condenser. Reflux was obtained with a heating mantle and a 500 watt tungsten lamp was turned on the system. (The lamp was cooled via a small directed fan.) Reflux was obtained and followed by the appearance of a yellow color characteristic of bromine gas. The reaction was slowed by temperature decrease and allowed to go until the disappearance of the yellow color. The solvent was then pulled away and the oily residue, vacuum distilled at 115 $^{\circ}$ /1mm Hg. NMR signals were found at (Acetone- d_6) 4.6 δ (s, 2H), 7.3 δ (q, 4H). Infrared absorbances were found at (CCl_4) 3400 (w), 3000 (b), 2280 (vb), 1910 (w), 1790 (w), 1770 (w), 1610 (s), 1585 (s), 1530 (s), 1445 (w), 1420 (w), 1290 (w), 1230 (s), 1210 (s), 1150 (s), 1110 (s), 1025 (w), 1000 (w), 840 (s), 820 (s), 770 (s), 760 (s), 730 (w), 710 (w), and 600 (w) cm^{-1} .

m-Bromomethyl phenyl isocyanate, 86.

m-Tolyl isocyanate (10 g, 0.047 mol), 1,3-dibromo-5,5-dimethylhydantoin (5 g, 0.0174 mol) and benzoyl peroxide

(0.16 g, 0.00068 mol) were added to 100 ml carbon tetrachloride in a flamed 125 ml flask with efficient reflux condenser with calcium chloride drying tube. Reflux was established and the reaction illuminated with a 500 watt tungsten lamp. A red brown color appeared in ten minutes after which the reaction was allowed to reflux approximately one hour. At that time the color was gone. The solvent was then evaporated away and the remaining oil vacuum distilled. The desired product came over at $108^{\circ}\text{C}/3.5$ mm Hg. NMR signals were found at (CCl_4) 4.35 δ (s, 2), 7.15 δ (m, 4). Infrared absorbances were as those found for the para compound. Strong isocyanate absorbance at 2280 cm^{-1} .

1-Ethoxycarbonyl-4-(m-bromomethylphenyl)-semi-carbazide.

m-Bromomethylphenyl isocyanate (9 g, 0.042 mol) in CHCl_3 was added dropwise to 3.1 g (0.0297 mol) ethyl carbazate in CHCl_3 cooled to -30° in a 250 ml flask equipped with a mechanical stirring, addition funnel and cold range thermometer. Addition was such that temperature was not allowed to raise above the -30° mark. Temperature was maintained with dry ice acetone bath below the flask. The semi-carbazide formed at this temperature and dropped out of solution as a white fine powder. The reaction was stopped and the solid filtered, washed with fresh CHCl_3 and dried in a vacuum oven. NMR of this product shows it to contain water. Recrystallization from anhydrous ethyl ether removed this, m.p. $128-30^{\circ}\text{C}$. Infrared absorbances were found at (Nujol) 3320 (b), 2900 (b, Nujol), 1760 (s), 1710 (w), 1690 (w), 1640 (s), 1600 (w),

1560 (m), 1510 (w), 1460-1440 (s, Nujol), 1380 (s), 1300 (s), 1240 (m), 1215 (m), 1160 (w), 1060 (w), 1030 (s), 890 (w), 800 (w), 750 (w), 720 (w), 700 (s). NMR signals were found at (Acetone- d_6) 1.2 δ (t, 3), 4.15 δ (Q, 2), 4.55 δ (s, 2), 7.4 δ (m, 5), 8.0 δ (s, 1), 8.4 δ (s, 1).

Anal. Calcd. for $C_{11}H_{14}N_3O_3Br$: C, 41.77; H, 4.43; N, 13.29. Found: C, 41.05; H, 4.89; N, 13.43.

Attempted synthesis of 1-ethoxycarbonyl-4-(p-bromomethyl-phenyl)-semi-carbazide, 89.

Ethyl carbazate (10 g, 0.11 mol) was added via addition funnel to the carbon tetrachloride solution containing the undistilled isocyanate obtained above in hopes of obtaining a semicarbazide mixture which could be easily purified. The temperature was maintained at 20° throughout the addition. A solid appeared which did not go into solution on heating to 60°C. This solid was filtered at this temperature to keep any unreacted carbazate in solution. The resulting greenish solid proved impossible to purify. NMR indicated it to consist of mostly brominated semicarbazide.

This reaction was repeated using the freshly distilled p-bromoethylphenyl isocyanate (6 g, 0.035 mol) and 3.4 g (0.040 mol) ethyl carbazate. A fine white powder was obtained which turned pale green after drying in a vacuum dessicator. NMR signals were found at (Acetone- d_6) 1.25 δ (t, 3H), 4.1 δ (Q, 2H), 4.6 δ (s, 2H), 7.4 δ (Q, 4-5H). Infrared absorbances were found at (Nujol) 3330 (m), 3200 (w), 3160 (w), 2950 (broad, Nujol), 1710 (s), 1680 (s), 1630 (s),

1620 (s), 1570 (s), 1520 (s), 1470 (m), 1420 (w), 1380 (s), 1330 (w), 1300 (w), 1250 (m), 1200 (w), 1190 (w), 1060 (w), 1020 (w), 900 (w), 850 (s), 690 (w), 660 (w), and 600 (w) cm^{-1} .

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_3\text{O}_3$: C, 40.26; H, 4.53; N, 13.74.
Found: C, 38.78; H, 4.72; N, 12.66.

Attempted bromination of p-tolylurazole.

4-p-tolylurazole (1.5 g, 0.00515 mol) was mixed with 2.24 g (0.0078 mol) ethyl carbazate and 0.46 (2×10^{-4} mol) benzoyl peroxide in 150 ml carbon tetrachloride. This system was heated to reflux and illuminated with a 500 watt tungsten lamp. The urazole was oxidized over a period of five minutes as the temperature was raised to reflux resulting in a brilliant red solution color. Reaction was allowed to continue for one hour. At that time, the solution was filtered and solvent evaporated away. NMR of the crude red solid indicated some bromination had taken place by the appearance of a signal at 4.45 δ . Sublimation resulted in obtaining only the non-brominated product.

Attempted bromination of p-tolyltriazolinedione, 77.

p-Tolyltriazolinedione, 77 (1.0 g, 0.00346 mol) was mixed with 0.5 g (0.0017 mol) 1,3-dibromo-5,5-dimethyl-hydantoin and 0.14 g (0.0004 mol) benzoyl peroxide in 500 ml CCl_4 in a 100 ml three necked flask with condenser and magnetic stirring. The system was irradiated with a 500 watt tungsten lamp while refluxing for 24 hours. NMR of aliquots taken at 6, 12, 18 and 24 hours show appearance of only a small amount of brominated compound by appearance of a signal at 4.4 δ .

γ -Chloropropyl isocyanate, 82

Sodium azide (33 g, 0.5 mol) was added to 150 ml distilled water in a 500 ml round-bottomed flask equipped with a mechanical stirrer, thermometer, addition funnel and cold water condenser. 4-Chloro-butylchloride (50 g, 0.44 mol) in 150 ml toluene were added to the aqueous azide solution dropwise. Temperature was maintained at 10-15° via ice bath and controlled addition rate. Within a few minutes, the clear organic layer became pale red-brown in color. After six hours, the reaction was stopped and the organic layer separated in a 500 ml separatory funnel and washed four times with a 10% Na_2CO_3 -ice water solution. This was stored overnight over CaCl_2 in the refrigerator. The azide solution was filtered and placed in a 500 ml three-necked flask with condenser. This was heated slowly to 80° with an oil bath. (Gas evolution became violent at times - recommend dropwise addition of azide solution to the pre-heated solvent to effect controlled rearrangement) Rearrangement is followed via infrared of a drop on NaCl plates as azide peak diminishes and isocyanate increases. The product was vacuum distilled at 54°/14mm Hg (Lit.⁶⁹ 54.6°/16mm).

1-Ethoxycarbonyl-4-(γ -chloro)-propyl semi-carbazide, 83.

Ethyl carbazate (5 g, 0.052 mol) dissolved in 75 ml toluene was added to a flamed 250 ml three-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser with CaCl_2 tube and addition funnel. A solution of 6.3 grams γ -chloropropyl isocyanate in 75 ml dry toluene was

added to the carbazate solution with stirring while the temperature was maintained at 10-20°C. A white gelatinous slurry forms rapidly. After complete addition, the mixture was refluxed for 20 minutes. The cooled gel became a white precipitate overnight, m.p. 103-105°C. NMR signals were found at (DMSO-d₆) 1.2δ (T, 3), 1.8δ (m, 2), 3.2δ (Q, 2), 3.7δ (T, 2), 4.1δ (Q, 2), 6.4δ (T, 1), 7.7δ (s, 1), 8.7δ (s, 1).

Anal. Calcd. for C₇H₁₄N₃O₃Cl: C, 37.59; H, 6.31; N, 18.79. Found: C, 37.66; H, 6.38; N, 18.77.

Attempted cyclization of 83 with 4M KOH.

The semi-carbazide, 83, (1.0 g, 0.004 mol) was mixed with 5 ml 4M KOH with rapid stirring until solubilization was attained. This was heated to 50°C for 20 minutes, then cooled with an ice bath. The cooled solution was acidified slowly maintaining a temperature of 10-15°C. At the neutralization point, vigorous CO₂ effervescence was noted, an indication that cyclization did not occur.

Attempted cyclization of 83 with NaOet.

The semi-carbazide, 83, (4.0 g, 0.018 mol) was mixed in a round-bottomed flask with 300 ml ethanol (absolute) to which 6.0 g (0.13 mol) of a filtered 50% oil dispersion of NaH in 50 ml ethanol (absolute) had been added. The solution was refluxed for three hours during which time, clear orange solution became cloudy with a very fine precipitate which was determined to be NaCl, indicating displacement was taking place at the γ position.

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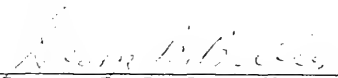
Biographical Sketch

Author Grady Williams, III was born in Atlanta, Georgia on November 6, 1946 and moved in that year to Valparaiso, Florida. In 1967 he moved to Paxton, Florida. He graduated from the Bolles School in June of 1965. He attended undergraduate school at Tulane University. As an undergraduate he was a member of Alpha Tau Omega social fraternity and Alpha Phi Omega service fraternity. He served as a dormitory advisor his sophomore and junior years and as a student academic advisor his junior year.

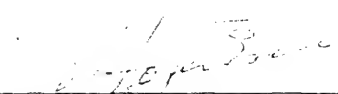
In June of 1969 he enrolled in the graduate school at the University of Florida. He joined the Alabama Army National Guard in August of 1970.

In December, 1972 he married Patricia Raines of Little Rock, Arkansas.


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~~July~~
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